THE

# CHEMICAL NEWS

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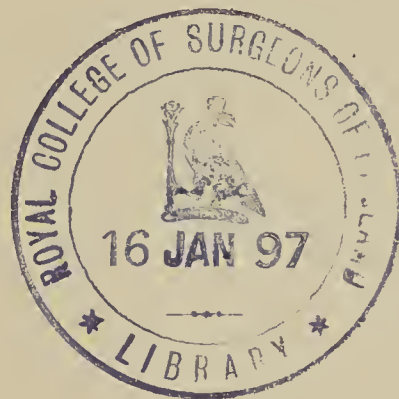## JOURNAL OF PHYSICAL SCIENCE.

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## PHARMACY, ARTS, AND MANUFACTURES.

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## WILLIAM CROOKES, F.R.S., &c.

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## ACTION OF ACETYLENE UPON IRON, NICKEL, AND COBALT, REDUCED BY HYDROGEN.

### By HENRI MOISSAN and CH. MOURET.

BERTHELOT has been the first to establish that the alkaline metals, if slightly heated along with acetylene, yield acetylides decomposable in the cold by water, with the reproduction of gaseous acetylene.

On repeating the same experiment in presence of iron, Berthelot obtained a rapid destruction of acetylene, with a formation of empyreumatic carbides with coke and hydrogen, without a production of iron acetylide.

The existence of nickel carbonyl has led us to resume the action of acetylene in the cold upon certain metals prepared in a state of great porosity.

Iron, nickel, and cobalt have been obtained on reduction by hydrogen at the lowest temperature possible. For the precaution to be taken in this preparation see the memoir in the *Annales de Chimie et de Physique*, by H. Moissan (1880).

A Kipp's apparatus containing pure calcium carbide, prepared in the electric furnace, enabled us to have a regular delivery of gaseous acetylene. This gas, after being washed with water and passed into a flask filled with anhydrous glycerin, was then dried over calcium chloride and potassa recently fused in a silver crucible.

A three-way cock enabled us to cause the acetylene gas to arrive abruptly upon the reduced metal. This latter was arranged in a tube which was filled with hydrogen or which could be exhausted.

Under these conditions, as soon as the acetylene gas was present in large excess, there was produced a very lively incandescence on contact with the metal at the ordinary temperature of the laboratory. Abundant fumes appeared in the tube, and condensed in the cold parts of the apparatus. If the speed of the gaseous current was slackened the incandescence ceased, but reappeared as soon as it was again accelerated.

If the reduction of the metal has not been effected carefully, and at the lowest temperature possible, the reaction may not be produced; but it is sufficient to heat any point of the tube with a spirit-lamp to see the phenomenon appear distinctly. The incandescence then gradually spreads over a length which may extend to 15 to 20 c.m.

This incandescence does not last more than from two to three minutes; at the moment when a plentiful deposit of carbon is formed in the tube the obstruction is complete, the gaseous current is arrested, and the luminous points disappear.

This experiment is especially brilliant with iron, but it is also produced very distinctly with nickel and cobalt reduced with hydrogen.

The black powder which is found accumulated in the tube after the experiment consists of a light carbon, in which the metal is diffused. It resembles the ferruginous carbon studied by Grunner (*Annales de Chimie et de Physique*, Series 4, vol. xxvi., p. 8, 1872) in the reduction of iron oxides by carbon monoxide. This coal evolves hydrogen, and leaves a black ferruginous residue. This carbonaceous residue is so much the richer in metal as it is nearer to the reduced iron employed in the experiment.

The very dense vapours produced at the moment of the reaction may be easily condensed by means of a small glass worm bedded in ice. The liquid thus obtained is rich in benzene, this latter substance being accompanied by all the carbides which can be produced in this reaction, the formation of which has been studied by M. Berthelot.

Lastly, we have studied the gases produced, and observed that, as long as incandescence does not take place, the acetylene is not modified. No products condensible at −23 are formed, and the properties of the gas are not at all altered.

As soon as the reaction at any point extends to ignition the gas collected is pure hydrogen, as appears from the following analyses:—

|         | Gas, c.c. | After the cuprous reagent. | Acetylene, per cent. |
|---------|-----------|----------------------------|----------------------|
| Nickel  | 6·8       | 6·5                        | 4·4                  |
| ,,      | 6·8       | 6·5                        | 4·4                  |
| Cobalt  | 10·4      | 9·5                        | 8·6                  |
| Iron    | 6·9       | 6·8                        | 1·4                  |
| ,,      | 7·0       | 6·9                        | 1·4                  |

The gaseous residue, after treatment with copper subchloride, is pure hydrogen. Eudiometric combustions have yielded us many quantities of carbonic dioxide scarcely appreciable, derived from a small quantity of vapour of benzene.

It results from these experiments that acetylene reacts at ordinary temperatures upon reduced iron, nickel, and cobalt, producing a great disengagement of heat. A portion of the acetylene is transformed, conformably to

the pyrogenous reaction described by M. Berthelot, into benzene and its polymers, whilst the chief part of the gas is split up into its elements, carbon and hydrogen.

This reaction is due to a physical phenomenon. The reduced iron, nickel, and cobalt are extremely porous, and absorb acetylene energetically. This absorption liberates a quantity of heat, which occasions the polymerisation, and ultimately the decomposition of the acetylene. Hence all the energy reserved in the acetylene (an endothermic compound, as M. Berthelot has established) becomes available. The totality of these reactions produces incandescence, and the phenomenon continues, becoming more and more accentuated until the carbon derived from the decomposition of the acetylene accumulates in the tube in a quantity sufficient to stop the afflux of the gas.

If this interpretation is correct every porous substance, such, e.g., as platinum, should yield an identical result. This, in fact, we have been able to establish.

Platinum black was prepared by reducing platinic chloride with sugar in presence of solution of sodium carbonate. After washing with hydrochloric acid, and then successively with water, alcohol, and ether, it was dried *in vacuo* over sulphuric acid.

This platinum-black was arranged in a tube of Bohemian glass, in which a vacuum had been made with the mercury pump. As soon as the acetylene came in contact with the platinum black, the latter became incandescent, and the reaction was produced as already described,— deposit of carbon, formation of hydrogen and of pyrogenous carbides.

Platinum sponge and platinised asbestos act in the same manner. If the phenomenon does not appear at once, it may be induced by applying a slight heat.

These essentially porous substances behave, therefore, like iron, nickel, and cobalt.

Finally, on diluting acetylene with an inert gas, such as nitrogen, we may hinder the production of incandescence, but the absorption of the gas nevertheless takes place slowly, and by degrees the metal is carbised and retain a little hydrogen.

We have not been able, under these conditions, to isolate any solid or liquid compound containing metal.

In conclusion, we may say that pyrophoric iron, nickel, and cobalt, i. e., reduced at the lowest possible temperature and placed in contact with an excess of acetylene in the cold, decompose this gas with incandescence, producing charcoal, hydrogen, and pyrogenous carbides. This decomposition must be ascribed to a physical phenomenon—the porosity of the metals. The same phenomenon is observed with platinum sponge.—*Comptes Rendus*, cxxii., p. 1240.

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## SEPARATION OF SILVER FROM GOLD BY VOLATILISATION.

By Dr. JOSEPH W. RICHARDS, of the Lehigh University.

IN making the quantitative blowpipe assay for gold and silver, it is usual to treat 100 m.grms. of ore at a single fusion, yielding buttons which are too small to be weighed accurately, but whose weight must be found by measuring carefully their horizontal diameters.

As determined by Plattner (and often verified in the writer's experience), silver buttons weigh 0·6346 of the weight of spheres of silver of the same diameter as measured, and gold buttons 0·7506 of the weight of gold spheres. The buttons obtained usually weigh 0·5 to 1·5 m.grms. and the separation of the silver from the gold in buttons so small is a matter of considerable difficulty. Plattner remarks that no satisfactory method of separation in the dry way is known, and recommends the parting by nitric acid. Working, however, with buttons smaller than pin-heads, it is extremely difficult to boil two or

three times with nitric acid, to wash until the silver salt is all removed, and then to gather and melt down the gold, without losing a considerable proportion of the gold in three or four directions.

Knowing that, on long heating, silver gives a coating of oxide on charcoal, and that gold does not, I made experiments to determine whether silver could be thus separated from gold, and have found the method practicable. On heating to a bright yellow heat (not to whiteness) upon charcoal an alloy of gold and silver, before a sharp-pointed oxidising flame, the silver volatilises easily and steadily until there is less than 5 per cent of silver remaining in the gold. I estimate this volatilisation to take place a little above the melting point of copper, say at 1100—1200° C. To remove the remainder of the silver, the heat is raised nearly to whiteness, or to about the melting-point of steel (1500° C.). When the silver is entirely eliminated, the gold, at this temperature, begins to volatilise also ; in fact, a trace of gold will be carried off with the last of the silver, and if the ash of the charcoal be white it will show a faint crimson coating close to the assay. When this coating is heavy enough to be seen without the use of a lens, the silver has been completely volatilised, and the remaining button is pure gold. The amount of gold necessary to give this coating is too small to be determined by weighing or measuring.

Having explained the principle made use of, I will give the further details of conducting the operation. The charcoal should be dense, so as not to burn away too quickly. Too light a charcoal will not stand the five or ten minutes' application of the oxidising flame without burning through the piece. It should also leave a white ash under the oxidising flame, so as to furnish a background on which to see the crimson gold coating which determines the end of the operation. I have found the dense, hard charcoal made by Johnson and Co., of New York, to answer these requirements admirably. It is well, also, to work with a porcelain saucer, or large sheet of clean paper, under the flame, to catch the button in case it should be blown from the charcoal.

In order to perform this separation without excessive exertion, I would recommend that a gas flame not over 2 centimetres high be used, that the tip of the blowpipe be advanced at least halfway through the flame, and inclined somewhat sharply downwards, at an angle of about 45°. By observing these simple directions, a very sharp-pointed, needle-like oxidising flame will be produced, about 1 centimetre in length to the blue tip, which I have found the best for the purpose in view. To produce this the blowing need not be strong, but it should be kept up steadily. The button, in a shallow cavity near the end of the stick of charcoal, is now brought directly in front of the point of the flame, at about 1 to 2 millimetres from the visible blue tip. Its position, of course, is regulated by the temperature observed. The button should not, at this stage, be heated to whiteness, else the silver will boil and cause a loss by sputtering. The charcoal is held inclined towards the flame at an angle of about 30°, so that the flame descends almost vertically upon the button, and thus decreases the liability of its displacement by the force of the blast.

It will be found practicable to continue a blowing for about three minutes without discomfort, at the end of which time the operator may stop to observe the colour of the button. Supposing the alloy, on starting, to have been white, it will usually become pale yellow in from three to six minutes. When the alloy exhibits a brass-yellow colour, the heat should be raised, and the next blowing continued for not over two minutes. At the end of this time the alloy will usually exhibit nearly the pure gold colour, but no gold coating, or, at most, only a trace of it will be seen on the charcoal. After this, the heat should be raised to nearly whiteness, and then continued for not over one minute at a time. If a faint gold coating appears, further heating for one minute will usually develope a distinct crimson coating, visible without

the lens, and the alloy will show the pure gold colour. It is then taken out, cupelled, and measured.

If the amount of gold present be very small, it is difficult to continue volatilising silver after the button gets smaller than ¼ millimetre in diameter. The difficulty is caused by the ash of the charcoal, which, fusing to a slag, envelopes the button. To continue the removal of the silver, should the button arrive at this size without showing the gold colour, the operator cupels and measures a pure gold button of about the same size and adds it to the button being treated. The enlarged button is now worked down to pure gold, as before, removed, cupelled, and measured. The weight of gold obtained is diminished by the amount added, the difference giving that in the ore.

If the heating to incipient whiteness be continued two or three minutes after the visible gold coating is obtained, a very pretty gold coating of bright, peach-blossom colour is obtained, and a sensible amount of gold is lost by volatilisation. A pure gold button, 1 millimetre in diameter, weighing 7·58 m.grms., lost 0·03 m.grms. (0·4 per cent) each minute that it was heated to whiteness, and in five minutes gave a beautiful crimson coating. A silver button of similar size lost 18 per cent of its weight, each minute, at only a bright yellow heat. I estimate the point at which gold begins to volatilise as about the melting-point of soft steel (1500° C.). It is certainly considerably below the melting-point of platinum (1775° C.).

In conclusion, I wish to say that I have tested this method of separation in many different ways, with large and small buttons, and upon alloys rich and poor in gold, and have found the separation to be absolute when the conditions above described are properly observed. I have repeatedly alloyed a gold button with different amounts of silver, and then driven off the silver, the button, after two or three of such separations, remaining of exactly the same size and weight as at the start. In proposing this method of separation, I do not wish to disguise the fact that, to ensure success, it demands a steady hand and an experienced operator, and some practice ; but I believe that any one who has mastered the art of blowpiping sufficiently to make gold and silver assays, can, in a short time, master this method of separating the gold and silver.

(In the discussion of the above paper, it was suggested that the method might be practicable in the ordinary assay of gold and silver, as, at assay offices, if an electrically heated furnace could be devised, in which the buttons could be placed on suitable supports, and kept at the proper temperature to volatilise silver, with a current of air passing over them. The movement to the hottest part of the furnace would suffice to remove the last traces of silver, just as the last traces of lead are removed in cupellation in an ordinary muffle. The process of removing the silver would then resemble cupellation in its general outlines, except that the temperature would be about 300° to 500° higher).—*Journal of the Franklin Institute*, June, 1896.

# THE IODOMETRIC DETERMINATION OF SELENIOUS AND SELENIC ACIDS.*

By F. A. GOOCH and A. W. PEIRCE.

IT has been shown in a recent paper from this laboratory (Gooch and Reynolds, *Amer. Journ. of Science*, l., 254) that the simple contact of solutions of selenious acid, potassium iodide, and hydrochloric acid, according to the recommendation of Muthman and Schæfer (*Ber. d. Chem. Gesell.*, xxvi., 1008) is not enough to effect the liberation of the theoretical amount of iodine when the assump-

tion is made that the selenium of the selenious acid is all reduced to the elementary condition. On the other hand, it was found that the yield of iodine is complete when such mixtures are submitted to distillation under well-defined conditions. It is necessary, however, to estimate not only the iodine which passes to the distillate, but that which is retained in small proportion in the residue, and, though this method of proceeding yields closely accurate analytical results, and is by no means difficult, it is obvious that a process so contrived that the reduction of the selenious acid should be registered entirely in the residue would possess the advantage in point of convenience. We have made the attempt, therefore, to apply in this case a principle of action laid down in a method elaborated in this laboratory for the estimation of chlorates (Gooch and Smith, *Amer. Journ. of Science*, xlii., 220). When a solution of arsenic acid containing potassium iodide and sulphuric acid is boiled under defined conditions (Gooch and Browning, *Amer. Journ. of Science*, xxxix., 188) the arsenic acid is reduced to arsenious acid with liberation of iodine. When the arsenic acid is in excess the whole of the iodine is evolved and the arsenious acid produced is its exact measure. Upon making the solution alkaline with acid potassium carbonate, the arsenious acid may be re-oxidised by standard iodine, and the amount of iodine thus used will be the exact equivalent of that set free in the reduction process. If, however, any other substance more easily reducible than arsenic acid is present, such substance should, naturally, take its part in liberating iodine from the iodide, and the reduction of the arsenic acid should be correspondingly less. This was found to be the case when a mixture containing a chlorate, arsenic acid, potassium iodide, and sulphuric acid was boiled under regulated conditions, so that, with a knowledge of the amount of iodide employed and the determination of the quantity of iodine necessary to re-oxidise the arsenious acid produced, the data were at hand for calculating the amount of chlorate present in the mixture. It was our hope (which proved to be well founded, as the sequel shows) that selenic acid would behave like a chlorate under similar conditions.

Pure selenium dioxide was prepared by oxidising presumably pure selenium in strong nitric acid, evaporating the solution to dryness, dissolving the residue in water, treating the solution with barium hydroxide until precipitation ceased, filtering, evaporating the filtrate to dryness, subliming the selenium dioxide from the residue, and re-subliming that product in a current of dry oxygen (which we found to be vastly more convenient and effective than dry air) until it was perfectly white and crystalline. From the oxide thus made a standard aqueous solution was prepared, from which portions were measured and (for the sake of greater accuracy) weighed for use in the experiments to be detailed. To each weighed portion of the selenious acid, contained in an Erlenmeyer flask of 300 c.m.³ capacity, was added a weighed amount of potassium iodide (somewhat in excess of that theoretically required) prepared in solution of convenient strength and tested as to its reducing power upon arsenic acid under the conditions of the experiments ; a solution containing about 2 grms. of pure di-hydrogen potassium arseniate was introduced ; and finally 20 c.m.³ of sulphuric acid of half-strength. Protected from ordinary mechanical loss by a trap (consisting of a two-bulbed drying tube, cut short and hung loosely, with the wide end downward in the mouth of the flask), and from violent ebullition by the introduction of a few bits of porcelain, the liquid was boiled until the volume decreased according to indicating marks on the flask from 100 c.m.³ or more to 35 c.m.³, concentration to about this lower limit having been found to be necessary to the completion of the reaction. The residue was cooled, the acid was nearly neutralised with potassium hydroxide, acid potassium carbonate was added until it was present to the amount of 20 c.m.³ of its saturated solution in excess of the

quantity needed to complete neutralisation, and, after the addition of starch, standard iodine was introduced until the starch-blue appeared. The iodine introduced measured the arsenious acid (and so the quantity of iodine set free by the arsenic acid), and the difference between it and the iodine originally present in the form of the iodide represents the amount set free by the selenious acid.

The following table comprises the details and results of a series of determinations made in the manner outlined:—

$$Se = 79\cdot1, \quad O = 16.$$

| Initial volume. C.m.³ | Final volume. C.m.³ | $H_2SO_4$ half-strength. C.m.³ | Di-hydrogen-potassium ar-seniate. Grm. | KI taken. Grms. | $SeO_2$ taken. Grm. | $SeO_2$ found. Grm. | Error. Grm. |
|---|---|---|---|---|---|---|---|
| 100 | 35 | 20 | 2 | 1·3277 | 0·1280 | 0·1275 | 0·0005 − |
| ,, | ,, | ,, | ,, | 1·0429 | 0·0998 | 0·0994 | 0·0004 − |
| ,, | ,, | ,, | ,, | 1·0887 | 0·1024 | 0·1028 | 0·0004 + |
| ,, | ,, | ,, | ,, | 1·0405 | 0·1036 | 0·1028 | 0·0008 − |
| ,, | ,, | ,, | ,, | 1·0721 | 0·1030 | 0·1029 | 0·c001 − |
| ,, | ,, | ,, | ,, | 0·9958 | 0·1273 | 0·1272 | 0·0001 − |
| 125 | ,, | ,, | ,, | 2·0828 | 0·1997 | 0·2000 | 0·0003 + |
| ,, | ,, | ,, | ,, | 2·2272 | 0·2110 | 0·2113 | 0·0003 + |
| ,, | ,, | ,, | ,, | 2·1535 | 0·2067 | 0·2069 | 0·0002 + |
| 150 | 40 | ,, | ,, | 2·6554 | 0·2560 | 0·2549 | 0·0011 − |
| 175 | 35 | ,, | ,, | 3·2428 | 0·3110 | 0·3118 | 0·0008 + |
| ,, | 35 | ,, | ,, | 3·2428 | 0·3085 | 0·3083 | 0·0002 − |

Obviously the reduction of selenious acid by this method is regular and accurate.

When similar treatment was applied to selenic acid, it became apparent that the arsenic acid attacked and destroyed the iodide before the selenic acid had been completely reduced. It is plain, therefore, that the selenic acid must be reduced to the condition of selenious acid before its estimation by the iodide method can be attempted. Ordinarily the simplest mode of reducing selenic acid is by boiling it in solution with hydrochloric acid of definite strength (Gooch and Evans, *Amer. Journ. Sci.*, 1., 400), but in this case the presence of hydrochloric acid is precluded on account of the consequent volatilisation of arsenious chloride during the process of concentration in the subsequent treatment with the iodide. It has been shown, however, in a recent paper from this laboratory (Gooch and Scoville, *Amer. Journ. Sci.*, 1. 402), that selenic acid is easily and completely reduced to selenious acid by potassium bromide and sulphuric acid under defined conditions. Moreover, arsenious bromide is not volatilised appreciably under the conditions. We made the attempt, therefore, to effect the iodometric determination of selenic acid by first reducing it to selenious acid by the bromide process, and then treating the residue with arsenic acid and potassium iodide in the manner described.

Selenic acid was prepared in standard solution by treating a known weight of pure re-sublimed selenium dioxide by a strong solution of potassium permanganate, in presence of a moderate amount of sulphuric acid, until the purple colour was distinctly visible, dissolving the precipitated oxide of manganese by oxalic acid, again adding permanganate until the final colour of faintly visible pink was permanent for a half-hour or more, and diluting to a fixed volume. Portions of the solution of selenic acid were measured into counterpoised Erlenmeyer flasks of 300 c.m.³ capacity and weighed, 1 glm. of potassium bromide was added, and sulphuric acid in such quantity that the total amount of the free acid should correspond to 20 c.m.³ of the acid of half-strength. The solution possessing a volume of 60 c.m.³ to 100 c.m.³ was boiled until the clear colourless solution left when the bromine vanished began to colour again. Experience

showed that the reappearance of the brownish colour is very easily seen, and that it is not safe to conclude that all free bromine has been eliminated, under the conditions of dilution and proportion, until this stage of concentration—which corresponds to a volume of about 35 c.m.³—has been reached; but the distillation should not be pushed beyond the point at which the returning colour is noted. When this condition was reached the solution was cooled, and treated exactly in the manner described for the reduction of selenious acid. The neutralisation by acid potassium carbonate, after the final boiling, generally occasioned the precipitation of manganous carbonate, but the precipitate did not interfere in the slightest with the titration which followed.

The following table comprises the determinations which were made to test the accuracy of the iodometric determination of selenic acid by the combined processes of reduction:—

| $SeO_2$ taken as $H_2SeO_4$. Grm. | KI used in second reduction. Grms. | $SeO_2$ found. Grm. | Error. Grm. |
|---|---|---|---|
| 0·0378 | 0·6306 | 0·0380 | 0·0002 + |
| 0·0378 | 0·5643 | 0·0374 | 0·0004 − |
| 0·0516 | 0·7136 | 0·0517 | 0·0001 + |
| 0·0503 | 0·7302 | 0·0508 | 0·0005 + |
| 0·0541 | 0·6671 | 0·0544 | 0·0003 + |
| 0·1007 | 1·3277 | 0·1011 | 0·0004 + |
| 0·1008 | 1·3277 | 0·1011 | 0·0003 + |
| 0·1007 | 1·2082 | 0·1005 | 0·0002 − |
| 0·1007 | 1·1684 | 0·1016 | 0·0009 + |
| 0·1007 | 1·0522 | 0·0999 | 0·0008 − |
| 0·1009 | 1·2679 | 0·1005 | 0·0004 − |
| 0·1031 | 1·1119 | 0·1032 | 0·0001 + |
| 0·1870 | 1·8720 | 0·1879 | 0·0009 + |
| 0·2014 | 1·9915 | 0·2020 | 0·0006 + |
| 0·2016 | 2·0745 | 0·2025 | 0·0009 + |
| 0·2059 | 1·8687 | 0·2064 | 0·0005 + |

It is plain, therefore, that selenic acid may be determined iodometrically with accuracy by first reducing it to the condition of selenious acid by treatment with potassium bromide in presence of sulphuric acid, in the manner described, and then completing the reduction to the elementary condition by the treatment with potassium iodide and potassium arseniate.

## GROUND MINERAL PHOSPHATE AS A FERTILISER.*

### By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

THE finely-ground mineral phosphate (apatite), according to experiments made in our laboratory at Ottawa, is but very slightly soluble in 1 per cent citric acid solution. Thus, my results, obtained when using such a solvent in the proportion of one part of phosphate to 100 of the solution, showed that when treating a finely-ground phosphate containing approximately 25 per cent of carbonate of lime, only 6·2 per cent of the total phosphoric acid was rendered soluble. In other words, 1·5 per cent, approximately, of phosphoric acid had passed into solution by this treatment. Science has, therefore, corroborated practice, in showing that the ground mineral phosphate cannot be regarded as an economical source of *available* phosphoric acid, though undoubtedly the fineness and specific hardness of the material largely determines its exact value in this respect.

*Chemical Experiments towards rendering available the Phosphoric Acid of Mineral Phosphate.*

From these results it became apparent that a previous treatment of the mineral phosphate was desirable and,

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* From the "Report on Experimental Farms to the Department of Agriculture, Canada."

indeed, necessary, if it was to be applied with a view to immediate returns.

To this end various experiments have been made in the laboratory of the Central Farm since 1893 towards a means of cheaply and effectively converting the phosphoric acid of ground phosphate into soluble and available forms, by means of the sulphates and bisulphate, and carbonates of the alkali metals. The first report on these experiments is contained in the Report of the Minister of Agriculture for 1893. It is there shown that the fusion of one part of finely-ground phosphate with the bisulphate of soda renders soluble a large proportion of phosphoric acid. Thus, in one instance, phosphoric acid equivalent to 38·49 per cent of apatite had been so converted. I may be allowed to quote from that report my conclusions as to the solubility of the phosphoric acid after ignition with the sulphates and bisulphates of soda and potash :—" I infer from these results (1) that any soluble phosphoric acid that may be formed during the ignition of the mineral phosphates with the sulphate of soda and potash, immediately re-combines in the presence of water to form tricalcic phosphate, and (2) that the ignition of the mineral phosphates with the bisulphates of soda and potash produces, according to circumstances, more or less soluble phosphoric acid.

" This latter conclusion is a very important one, since it is possible that by using the by-product, sodium bisulphate, an economical method for the treatment of mineral phosphates may be devised. It is scarcely necessary to add that such a process would prove of great value to Canada and Canadian agriculturists. Before an affirmative statement can be made regarding the commercial success of such a method for converting and utilising our phosphate, the cost of the raw materials and of the treatment, as well as the price obtainable for the manufactured article, must be taken into careful consideration."

Since 1893, further work had been done, the details of which have not yet been published. These latter experiments comprise the following :—(A) Heating together finely-ground phosphate and sulphate of soda, and treating the residue with 2 per cent of citric acid solution. The results showed that phosphoric acid equivalent to 35 per cent to 37 per cent of the phosphate had been dissolved.

(B) Ignition of the finely-ground phosphate with sodium bisulphate and treatment of the mass with 2 per cent citric acid solution. In this case 50 per cent of the apatite was found to have been rendered soluble in the acid solution.

The by-product that was used in these experiments contained only a small proportion of bisulphate, the larger part being sulphate of soda. It did not yield, therefore, as large an amount of soluble phosphoric acid as when pure bisulphate was used.

These experiments, the results of which I have condensed, were made before the appearance of Dr. Dyer's paper before referred to. Consequently, I was not then aware that 1 per cent citric acid represented the acidity in root sap. My solvent was undoubtedly too strong to give results which would allow us to say that the percentages of phosphate above stated are such as are rendered immediately available for plant use. Nevertheless, we may safely draw the conclusion that ignition of the finely-ground phosphate with sulphate of soda, as well as the by-product, bisulphate of soda, does convert a considerable amount of phosphate into a form much more readily available than the phosphoric acid in the untreated material.

I intend to repeat these experiments, using 1 per cent citric acid solution for the treatment of the ignited mass.

(C) The third series of experiments in this investigation conducted by us affords data regarding the effect of igniting finely-ground phosphate with (1) wood ashes and (2) carbonate of potash. A mixture of wood ashes and finely-ground phosphate was heated together, and the mass subsequently treated with water. In the aqueous extract, phosphoric acid equivalent to 1·25 per cent of the phosphate was found. The residue, after treatment with water, was left over night in a 1 per cent solution of citric acid ; this brought into solution phosphoric acid equivalent to 3 per cent of the phosphate. As the duplicate experiment in this trial closely agreed, we must infer that simple heating with wood ashes does not appreciably improve the solubility of the phosphoric acid in the mineral phosphate.

In the next experiment sand was added to the wood ashes and ground phosphate before ignition. This method was not found to increase the percentage of available phosphoric acid over that found in the preceding experiment.

Trials were then made by fusing together carbonate of potash and finely-ground phosphate. Treatment of the mass with water dissolved phosphoric acid equivalent to 6·5 per cent of the phosphate, and the subjection of the residue to the action in the cold of 1 per cent citric acid further dissolved phosphoric acid corresponding to 43·00 per cent of the phosphate.

From these experiments, I conclude that ignition with wood ashes does not materially increase the availability of the phosphoric acid in apatite, but that ignitition with carbonate of potash does so very materially. If commercially any of the processes that comprise heating ground phosphate with the sulphates and bisulphates or carbonates of soda or potash are practicable, undoubtedly we have a means of readily rendering more or less immediately available much phosphoric acid now locked up and well-nigh useless to agriculture.

I may point out that if the potash salt were used in the fusion, the resulting fertiliser would contain, in addition to the available phosphoric acid, another element of almost equal importance to farm crops, viz., potash.

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## ON CEMENTATED STEELS.

By SERGIUS KERN, M.E., St. Petersburg.

IN the CHEMICAL NEWS, vol. lxxiii., p. 192, we gave a description of our process for crucible-steel melting, with a note upon cementated steels, which are necessary for the process. We prepared the steels for trials, in the steel foundry of the St. Petersburg, Naval Port (New Admiralty), as follows :—

As we had no special furnace for cementation, we made experiments, using plumbago crucibles 13 inches high and 10½ inches in diameter instead of cementation-boxes. The crucibles were heated in ordinary crucible coke furnaces usually employed for copper melting. Two experiments were made, and each time about 50 pounds of cementated steel was obtained.

1. *Charging the Crucible.*—On the bottom was placed a layer of charcoal 4 inches in thickness ; next a layer of rounds, obtained from the punching of open-hearth steel ship-plates (0·18 per cent of carbon). On this layer 2 inches of charcoal were placed, next a layer of rounds, a layer of 2 inches of charcoal, a layer of rounds, and, finally, all the top was filled with charcoal. A burnt clay plug was fitted and well plastered with clay.

2. *Operation of Cementation.*—The crucibles were heated in the furnaces for four and a half hours, and during this time, at the middle of the operation, a fresh charge of coke was made. At the end of the operation, the lids of the furnaces were covered with clay all over the seams. The crucibles remaining in the furnace, to cool, for twenty-four hours. On opening the crucibles, all the three layers of punchings were found to be melted together, and an ingot was found at the bottom of the crucibles which could be easily broken, having an earthy-greyish fracture, with numerous spots of graphite.

Analyses of several pieces from this ingot made at the Obouchoff Steel and Cannon Works, St. Petersburg,

showed the metal to contain, on the average, 3·60 per cent of graphite and 0·56 per cent of carbon.

The cemented steel, mixed with soft wrought iron and other ingredients adopted in our process, was melted in crucible-steel furnaces, for the production of chisel-steel, the analysis of which is given in CHEMICAL NEWS, vol. lxxii., p. 192.

This process gives fair tool-steel for the works themselves, but certainly the process is not proposed for making high-class tool-steel for the trade. The cost of our steel in ready tools (forged at the Port) was about sixteen shillings per pood.

# A QUICK NITROGEN ABSORBENT FOR THE LIBERATION OF ARGON
AND
## MANUFACTURE OF METALLIC LITHIUM.

### By H. N. WARREN, Research Analyst.

THE preparation of metallic lithium, which has up to the present been procured only in small quantities by the aid of electric currents upon the chloride, &c., has lately been simplified to a large extent. The author recommends for the preparation of that substance an iron tubulated retort, into which is introduced a suitable quantity of perfectly dry lithia, LiHO, and heated by means of a charcoal furnace; metallic magnesium in small pieces is from time to time brought into contact with the same through the tubular of the retort. A somewhat violent action takes place, and metallic lithium distils over according to the following equation :—

$$LiHO + Mg = MgO + H + Li.$$
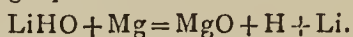
The carbonate may also be employed, but the metal is in the latter case accompanied by various quantities of lithium carbide, which, when thrown upon water, evolve acetylene gas.

As a nitrogen absorbent, either quick-lime or barium hydrate is saturated with a strong solution of lithia, ignited, and mixed with a sufficiency of magnesium powder, and the mixture allowed to reduce in an atmosphere of hydrogen gas at as low a temperature as possible. The resulting mass thus obtained contains metallic lithium in an extremely divided state, as also small quantities of barium or calcium, which has the power of absorbing nitrogen gas with the utmost facility, the mixture often becoming incandescent during the reaction.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

# ON A REACTION OF CUPROUS COMPOUNDS WHICH MAY SERVE FOR THE RECOGNITION OF THE NITRITES.

### By PAUL SABATIER.

IN contact with a solution of silver nitrate cuprous oxide totally displaces the silver, yielding a solution of cupric nitrate. After the solution of silver has been several times renewed there remains a grey matter, which Rose observed as far back as 1857 (*Poggendorff's Annalen*, vol. ci.), and which he considered as a mixture of metallic silver and an insoluble basic copper nitrate. On pursuing the study of this substance, which contains certainly not a cupric nitrate, but a cuprous nitrite, or a cuproso-cupric nitrite, I observed a special reaction, which I communicated, without explanation, at the meeting of the French Association for the Advancement of the Sciences, held at Bourdeaux, August, 1895. The grey matter, if carefully treated with an excess of concentrated sulphuric acid,

dissolves on it developing a magnificent violet blue colouration, which is immediately destructible by water, and which disappears spontaneously after the lapse of a few days.

A close examination of the reaction led me to conclude that the condition for its production is the simultaneous presence of concentrated sulphuric acid, of a nitrite, and a cuprous compound.

In order to obtain it the most conveniently, we dissolve suddenly a small quantity of dry crystalline sodium nitrite in concentrated sulphuric acid. If to the colourless limpid liquid thus obtained we add some quantities of red cuprous oxide, they immediately dissolve, yielding, along with a slight disengagement of nitric oxide, a very intense purple colour.

All the cuprous compounds, the bromide, iodide, chloride, hyposulphite, double cuproso-sodic, also all the cuproso-cupric compounds, such as the red sulphite and Schütte's violet blue ammoniacal hyposulphite, give the same reaction.

With dry cuprous chloride the action is not immediate, but it ensues after some time, with a certain escape of chlorine. The iodide yields a reaction which is not immediate, but very regular; nitric oxide is set at liberty, and all the iodine is eliminated in crystals, which may be removed by shaking the liquor with chloroform, which has no destructive action upon the purple matter.

Metallic copper obtained by reducing the pulverulent oxide with hydrogen acts strongly upon the nitrososulphuric liquid, and gives the violet colouration, with a very copious discharge of nitric oxide. Copper in sheets or turnings is only attacked after some time, and is surrounded with a violet sheath, which is gradually diffused in the liquid.

The cupric compounds give no reaction, nor is there any colouration with various metallic compounds of mercury, lead, silver, tin (stannous or stannic), manganese, cobalt, nickel, &c.

The same reaction may be produced with the solution of nitro-sulphuric acid, $SO_2(NO_3)OH$, in concentrated sulphuric acid, obtained in crystals by the action of sulphurous gas upon fuming nitric acid and suitably dried. But it is necessary to operate only upon solutions in a large excess of sulphuric acid.

*Properties of the Purple Solution.*—This solution, obtained with the cuprous compounds, is slowly decolourised, even if protected from air in a sealed tube. A rise of temperature favours the destruction, which is not immediate, even at 100°.

If shaken up in a flask with dry air it is promptly decolourised by oxidation, and a white precipitate of cupric sulphate is deposited. Oxidising agents, such as nitric acid, persulphuric acid, and lead peroxide, quickly produce the same result. Bromine decolourises it with production of black anhydrous cupric bromide.

Water, even if introduced with great care, so as to avoid a rise of temperature, destroys forthwith the violet compound. It is the same with sulphuric acid mixed with the fifth part of its volume of water.

*Use of Nitrous Acid as a Reagent.*—The reagent just described is a sensitive indicator of the nitrites. To detect the presence of a nitrite in a solution, we place he smallest possible drop on a white saucer, and upon it we place a drop of concentrated sulphuric acid, and we then let fall upon the liquid a few grains of cuprous oxide. If there is a nitrite, the violet tint appears at once.

The reaction, which is still very distinct with a solution containing per litre $\frac{1}{10}$ mol. of nitrous acid, is certainly less sensitive than that with metaphenylene-diamine.

The colouration is fugitive because the atmospheric moisture and oxygen contribute to its destruction. It is also interfered with by the presence of a notable quantity of nitrate.

In a future communication I shall show that the violet product obtained with the cuprous compound is simply the cupric salt of nitrosodisulphonic acid, a violet acid

which I have succeeded in preparing.—*Comptes Rendus*, cxxii., No. 24, p. 1417.

## OZONIFEROUS ALDEHYDS FOR THE DETECTION OF MINIMUM TRACES OF IODINE IN PRESENCE OF CHLORINE AND BROMINE.

### By E. LUDWIG.

IT has long been known that ethereal oils can take up ozone, and retain it for a long time in a state capable of reaction. As it will be seen from the following, most aldehyds under certain circumstance possess this attribute, and can in consequence eliminate iodine. With this we may connect an observation made by Anato. Not the slightest iodine reaction was obtained with an ethanal, para-ethanal propanal, methyl-propanal, or phenyl-methanal, if distilled in a current of carbonic acid, whilst a few drops of a distillation accompanied by a current of air suffice to show potassium iodide even in very dilute solutions.

For small quantities of iodine the sensitiveness of the reaction may be considered at least equal to the nitrite reaction. Even in solutions containing 1 part of iodine in 600,000 parts of water, the liberated iodine could be recognised as a permanent pale reddish colouration, if the smallest possible quantity of colourless carbon disulphide and a white background were employed.

I have tested the general applicability of the reaction, and found that it can be used successfully, although the solution must be neutral and contain no reducing agents, no mercurial salts, and no excess of the heavy metals.

It is a peculiar advantage of this reaction that even saturated solutions of bromides, free from iodine, do not react at all, whilst the presence of potassium iodide in a solution of 1/50,000 is sufficient, in spite of the bromides, to bring out plainly the reaction in carbon disulphide. The nitrite reaction fails already in solutions of 1/20 potassium bromide and 1/20,000 potassium iodide, so that the ozone-aldehyd reaction is about thirty times more sensitive.

A similar reaction is perhaps that recommended by E. Cook (*Chem. Society*, 1885, p. 471), in order to liberate iodine by hydrogen peroxide and acetic acid.

All aldehyds as yet examined, when pure, are alike capable of being used as reagents, and the only preparation needed is exposure to the air.

One c.c. of pure ethanal, poured into a 2-litre flask, could after an hour be used as reagent. After being kept for a day there was no considerable decrease of sensitiveness, but on the addition of water the reagent is decomposed in a very short time.

Para-ethanal, propanal, phenyl-methanal, can be at once obtained capable of reaction by distilling a small quantity, or the two latter by boiling up in a flask. In this state the normal aldehyds can retain their fitness for reaction, except methyl-propanal, which after a few hours requires to be again boiled.

Only the smallest possible quantities must be used From 2 to 5 drops are sufficient for each reaction, and must be added carefully. The reaction succeeds best with phenyl-methanal, if we use 4 to 8 drops of an emulsion obtained by mixing 10 drops of aldehyd with 10 c.c. of water in a dropping-glass.

For recognising the iodine set free we may use starch-paste or carbon disulphide; the sensitiveness is considerably greater with the latter.— *Berichte*, xxix., No. 9, p. 1454.

Alimentary Value of a Bread obtained from Flour sifted to different Standards.—Aimé Girard.—A refutation of the assertion that bread made from fine flour is of an inferior alimentary value.—*Comptes Rendus*, No. 23.

## RESEARCHES ON THE RÖNTGEN RAYS.[*]

### By ALFRED M. MAYER.

1. *The Röntgen Rays cannot be Polarised by passing through Herapathite.*

HERAPATHITE is an iodo-sulphate of quinine, discovered by W. B. Herapath in 1852 (*Phil. Mag.*, March, 1852), and named herapathite by Haidinger. Herapath gives several formulæ for its production. The one which succeeded the best with me in giving crystal plates of large area is contained in *Phil. Mag.*, Nov., 1853. It is as follows :—

| | |
|---|---|
| Bisulphate of quinine .. .. .. | 3'24 grms. |
| Pyroligneous acid .. .. .. .. | 56 c.c. |
| Alcohol (95 per cent) .. .. .. | 56 c.c. |
| Solution of iodine (1 grm. in 11 c.c. alcohol) .. .. .. .. .. | 50 drops. |

The bisulphate of quinine is added to the mixture of pyroligneous acid and alcohol, and heated to 55° C., and then the iodine is added drop by drop while constantly stirring the solution. The vessel containing the solution in then placed on several layers of thick felt resting on a firm support to prevent vibration, and it thus remains about eighteen hours at a temperature of 8° C. At the expiration of that time large crystals will generally be seen floating on the surface of the liquid, the majority being at the bottom of the vessel. The solution gives, of herapathite, only 1·15th of the weight of bisulphate of quinine.

As suggested by Herapath, a microscope cover-glass is cemented to the end of a glass rod, with its plane at right angles to the rod, and is carefully brought under the floating crystal, very slowly brought up to it, and the crystal is thus secured on the surface of the glass. The mother-liquid is then absorbed from the glass by blotting-paper. If several crystals are desired on a cover-glass, a glass tube closed by the finger is brought over the crystals at the bottom of the vessel, the finger removed, then replaced and the tube taken out of the liquid. The crystals are allowed to sink into the drop at the end of the tube by holding the latter for some time in a vertical position : the drop is then brought in contact with a cover-glass. This is the manner in which I placed on the glass discs and blotting-paper the plates of herapathite used in my experiments.

Röntgen has shown that generally the lower the density and always the thinner the substance, the less it screens from a photographic plate the action of the X rays. Herapathite is, therefore, eminently fitted as *the* substance on which to make experiments which are to decide whether the X rays can or cannot be polarised by having traversed crystals which, like herapathite and tourmaline, transmit only one polarised beam, the other being absorbed by the crystal, for the density of herapathite is 1·557, and plates of only 0·012 m.m. thick are sufficient to answer the question. When crystals of herapathite 0·012 m.m. thick have their optic axes crossed at 90°, these crossed portions viewed against incident light appear black, so powerful is the polarising property of this substance. If the X rays be polarisable these black portions should act like thick lead, and completely screen the sensitive film from the action of the X rays. The fact is the crossed herapathites do not screen the X rays any more than the herapathites do when superposed plates have their axes parallel. In the latter case the crystals freely transmit light with a faint olive green tint.

The thickness of crystal plates used in the experiments varied from 0·01 m.m. to 0·025 m.m., as found by focussing with a micrometer-screw a powerful objective on the top surface of the crystals and on the glass on which they rested.

[*] From the *American Journal of Science*, vol. i., June, 1896.

Six discs of glass, 0·15 m.m. thick and 25 m.m. in diameter, were covered with herapathites in the manner described. They crossed one another at various angles; where they crossed at 90° the crossed portions were black. On a piece of yellow blotting-paper, ¾ m.m. thick, were also placed several layers of herapathites, so deep that they reflected a green metallic lustre like the elytra of cantharides. These discs and the blotting-paper were fastened to the slide covering the photographic plate. This slide was impervious to two hours' exposure to the actinic action of the sun's light. On the slide were also three discs of thin glass, so overlapping that the X rays had to pass through 1, 2, 3 thicknesses of the glass before reaching the sensitive plate. These served as standards with which to compare the screening effects of the herapathites.

The slide so prepared and covering a sensitive plate was exposed to the radiations of a Crookes tube in three experiments, for ½, 1, and 2½ hours. On developing the plates, not the slightest trace of the presence of the herapathites was visible. The photographs of the glass discs had not the slightest mottling on their surfaces; appearing to the unaided eye and when examined through a magnifying glass with uniform illumination and grain throughout, and exactly like the photograph obtained by the X rays passing through a similar glass disc with nothing on its surface. The herapathites used in the experiments were so thin that they did not appreciably screen the X rays, whether the axes of the superposed crystals were parallel or crossed. But the action of the rays on the square of blotting-paper proved, even more conclusively, that the X rays cannot be polarised in this manner, for where this paper covered the photographic plate nothing was visible, except by careful scrutiny and with a favourable illumination, and then a mere ghost of the paper was detected, but with no traces whatever of the herapathites.

These experiments confirm in a convincing manner what Röntgen found by his experiments, viz., that the X rays cannot be polarised. At least, they cannot be polarised by passing through herapathite, which is by far the most powerful polarising substance known. It is unlikely that polarisation will be detected by using any doubly refracting substance which transmits two beams polarised in planes at right angles to each other; for if polarisation exist, the thickness of the substance required to get a measurable departure of the two rays so screens the X rays that a very small fraction of them (at least by calcite) will be transmitted; also, Röntgen is of the opinon that if the X rays be refrangible, the index of refraction is nearly unity even in such a highly refracting substance as ebonite, which has an index of about 1·6 ("On the Physical Properties of Vulcanite," by A. Mayer, *Amer. Journ. Sci.*, Jan., 1891), It is therefore reasonable to suppose that the difference in the refraction of the ordinary and extraordinary beams will be too small to be measurable in the faint shadowgraphs obtained by doubly refracting substances.

It remains to be decided whether the X rays can or cannot be polarised by reflection, Professor Rood having recently proved conclusively that they are reflected from platinum.

### 2. *The Density of Herapathite.*

Herapath gives 1·89, at 60° F., as the density of the very remarkable substance he discovered (*Phil. Mag.*, 1855, p. 369). As its density is interesting to have in connection with the experiments described above, I made two determinations of it by weighing about 0·3 gr. of the substance in water, and also by the displacement it gave of the water in a specific gravity flask. The mean of these two measures was 1·6. As this number differs greatly from that of Herapath, I thought that the small mass I had used was the cause of the discrepancy. I then made about 2 grms. of herapathite, freed it of its mother-liquid by washing with water at 0°, and dried it

at 25° *in vacuo*. When it had ceased to lose weight I weighed it in a specific gravity flask holding about 10 c.c., then just covered it with water, placed it *in vacuo* and agitated it, so that it would be freed of any air that might be contained in its mass. The flask was then nearly filled with water and again placed *in vacuo*, then entirely filled and weighed. I found from this carefully made experiment that the density of herapathite is 1·557 at 20° C.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.
*Ordinary Meeting, June 26th, 1896.*

Captain W. DE W. ABNEY, President, in the Chair.

Mr. F. BEDELL read a paper "*On Admittance and Impedence.*"

The author discusses the application of the method of "vector diagrams" to the solution of questions connected with alternating currents. He shows how, by a consideration of the *loci* of the different lines on such a diagram, many problems which require for an analytical solution a lengthy investigation, may be simply and expeditiously solved.

Mr. BLAKESLEY asked the author what was his test of resonance? Was it that the primary current and E.M.F. were exactly in the same or in opposite phase. The term resonance was an acoustical one, and he did not see why it should be applied to one particular case in the electrical problem.

Mr. INWARDS asked what degree of accuracy the author had obtained?

The author, in reply, said that if the applied E.M.F. and the current were brought into phase by means of a condenser in the secondary, then he called that a case of resonance. The agreement between the experimental and theoretical results was generally within from 1 to 3 per cent.

Prof. S. P. THOMPSON read a paper " *On the Properties of a Body having a Negative Resistance.*"

The author, after showing the consequences which would follow, according to the laws of Joule and Ohm, if we postulated the existence of a body having a negative resistance, goes on to show how the observations described by Messrs. Frith and Rodgers in a paper read at a recent meeting of the Society, only prove that that part of the resistance of an arc which is not constant is a positive resistance that varies inversely as the current. Since it varies inversely as the current, the term—

$$\frac{d\,\mathrm{R}}{d\,\mathrm{C}}$$

will be negative, and so will the quantity—

$$\mathrm{C}\frac{d\,\mathrm{C}}{d\,\mathrm{R}},$$

which is what they have tabulated as a negative resistance. That the resistance of the arc itself should vary inversely as the current is natural, for it may be regarded as a column of vapour, the cross section of which is proportional to the current, and therefore increasing in its conductances in direct proportion to the current. There is no need even to suppose any (distributive) adjuvant E.M.F., which would be the other alternative to the suggestion they have made.

Mr. SWINBURNE asked if the numbers on which Messrs. Frith and Rodgers based their arguments were obtained by taking successive readings of a voltmeter.

Prof. AYRTON said that what they maintained was, that it the arc acts as if it had a back E.M.F. and a

resistance, then the resistance is a negative quantity. In ordinary cases we do not know what really constitutes a resistance, but simply say that a circuit, in which electrical energy is being dissipated at a rate proportional to the square of the current, has resistance. If the loss is proportional to the first power of the current, then we say there exists a back E.M.F. Is it impossible to imagine a circuit in which a loss of electrical energy occurs proportional to the current and a return of energy to the circuit proportional to C ? If in a curve showing the relation between V and C you draw a tangent at any point, it is not the tangent of the inclination of this tangent which Messrs. Frith and Rodgers have called the resistance; it is another quantity which they call the electrical—

$$\frac{dV}{dC}.$$

In conclusion, the author seems to have based his paper on three misconceptions:—(1) That it had been claimed that a negative resistance could exist alone ; (2) that the curves given by Messrs. Frith and Rodgers showed that the ordinates were inversely proportional to the current ; (3) that what was measured was the geometrical—

$$\frac{dV}{dC}.$$

Mr. FRITH said that in a paper by Mr. Rodgers and himself they had defined the resistance of the arc as the ratio—

$$\frac{dV}{dA}, \text{ where, by } \frac{dV}{dA},$$

they meant not what was ordinarily understood by this expression, but the value of the ratio obtained by superposing an alternating current on a direct current arc. In order to show that, in cases analogous with that of the arc, but in which the true resistance can be verified, the electrical—

$$\frac{dV}{dC}$$

obtained by superimposing an alternating current gives correct results for the resistance, some experiments have been carried out. In one case a glow-lamp was placed in series with some fifty ampère secondary cells, and a current sent through against the E.M.F. of the cells. The value obtained for the electrical—

$$\frac{dV}{dC}$$

agrees very well with the value of the resistance obtained by dividing the P.D. between the terminals of the lamp by the current. At very low frequencies for the superimposed alternating current, it is evident that the electrical oscillations could travel along the steady valve curve ; and this is clearly the meaning of the critical frequency observed with cored carbons, namely, that under the critical frequency the superimposed alternating current travels on the steady valve curve, and over that frequency along the line joining the point on the curve and the instantaneous origin.

Mr. FRITH exhibited a mechanical model of the arc which he has devised. This model consists of two rods of carbon dipping in two mercury cups which are traversed by the current. The current also passes through a solenoid which attracts an iron core attached to the carbon rods, and draws them down into the mercury, thus reducing the resistance of the instrument. Hence it can be so arranged that the P.D. between the terminals decreases as the current increases. With this model it is found that, for superimposed oscillatory currents of such a frequency that the moving parts are notable to follow the changes in the current, the oscillations of the current and of P.D. are in phase, and the electrical—

$$\frac{dV}{dC}$$

gives the resistance of the apparatus for various currents.

Mr. CARTER asked the author how, in his vapour column theory, he explained the difference in the behaviour of solid and cored carbons.

Mr. ENRIGHT asked why it was absurd to suppose that a negative resistance could exist ? Prof. Ayrton and Mr. Frith had made in their definitions certain restrictions: it ought, however, not to be necessary to make such restrictions.

Mr. BLAKESLEY asked if, since the title of the paper by Messrs. Frith and Rodgers was entitled the "*True Resistance of the Arc*," it was to be inferred, as the results given were negative, that a negative ohmic resistance existed in the arc. Mr. Thompson's paper appeared to him (Mr. Blakesley) to be rather a mathematical than a physical paper.

Prof. RÜCKER said that the discussion showed that considerable confusion existed, and that the introduction of the term negative resistance only tended to fog matters. It was entirely wrong to argue that because you have a quantity with a positive value, therefore a negative value must also be possible. As an example, take the case of mass. If you defined as a positive mass that which is attracted to the earth, and then found that cork when immersed in water was repelled from the earth, would you, therefore, say that cork had a negative mass ? Is not " negative resistance " a term for which some equivalent could be found which would not lead to confusion ?

Mr. HOVENDON made some remarks on his experiments.

The author, in his reply, said that he did not dispute the accuracy of the results obtained by Messrs. Frith and Rodgers, but it was the interpretation that they had given of their results to which he objected. Mr. Frith now makes a new reservation, namely, that the results depend on the particular way in which the increment of C and the decrement of V are made. He supposes that, if the experiment is made in a particular way, a new slope is obtained which is proportional to what we call the true resistance, and hence gets a new definition of the quantity—

$$\frac{dV}{dC}.$$

He (the speaker) endorsed all Prof. Ayrton had said as to the interest of the model exhibited. The question is, Is there anything in the arc which acts as a source of energy to the circuit either as a negative resistance or as an adjuvant E.M.F. ? Mr. Frith's experiments do not give us any hint as to the point where the negative resistance occurs, and the absence of any such energy-giving portion of the arc, rendered probable by the fact that the arc itself is hotter than the crater. In reply to Mr. Carter, the anomalies which occur with cored carbons are so great as to prevent any argument being based on their behaviour.

The Chairman (Captain ABNEY) said that the mere fact that the quantity—

$$\frac{dV}{dC}$$

had been defined in two distinct ways showed that the definitions would have to be modified in some way.

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Process for Dissolving Ignited Iron Oxide and other Metallic Oxides. — Hugo Borntrager. — The methods used for re-dissolving ignited ferric oxide are, for the most part, circumstantial and tedious. The author generates hydrogen from hydrochloric acid and flower-wire (*i.e.*, the thin iron wire used by florists in making up bouquets, &c.), and adds the oxide in question. The oxide dissolves instantly, as the nascent hydrogen reduces it at once to ferrous oxide. The same holds good for many metallic oxides. The author is not in a position to say whether this procedure is available for determining the sulphur in burnt ores.—*Zeit. Anal. Chemie.*

## NOTICES OF BOOKS.

*Preserved Foods.* ("Les Conserves Alimentaires.")
By J. DE BREVANS, Chief Chemist at the Municipal
Laboratory of Paris. Paris: J. B. Baillière et Fils.
1895. 18mo., pp. 396.

Now the chief seats of dense population are precisely
those where the production of food is interfered with by
want of space or by ungenial climates and barren soils,
its preservation and transmission to the consumer must
decidedly rank with the more useful arts. Hence we
hold M. de Brevans as entitled to public gratitude for the
compilation of the work before us. The preservation of
foods involves questions of no little nicety. Decompo-
sition must be obviated; the escape of volatile consti-
tuents must be prevented, if thereby the flavour and
appetising character of the meats would be imperilled,
and digestibility and assimilability must not be sacrificed.
It is quite natural that a work of this character should be
undertaken in France, where, sooner than in many
countries, cookery has been recognised as an important
department of chemistry.

The subjects principally here considered are the pre-
servation of aliments of animal origin (butchers' meat,
fish, milk, butter, and eggs), that of aliments of vege-
table origin (vegetables and fruits), the decomposition
of preserved foods,—our French neighbours use a more
general term, "alteration,"—and the analysis of such
preserved foods.

The methods of preservation may be classed in four
groups :—

1. Procedures by desiccation and concentration.
2. Procedures by cold.
3. Procedures by sterilisation, with or without elimina-
   tion of atmospheric air.
4. Procedures by antiseptics.

Most of the preserved foods met with in commerce
have been produced by the joint action of two or more of
these methods, and none of them have come into
universal use. Liebig's extract of meat is, perhaps, most
widely known and used ; but the author remarks that the
true *rôle* of extracts of meat is to serve as condiments, to
enrich soup, gravy, &c., and they hence have but a slight
importance in domestic economy. An extract of mutton
produced in Australia has not given satisfaction.

The view of certain hygienists that extracts of meat
are positively injurious, is a view which is combatted by
Dr. Kemmerich.

Not a few extracts abundantly advertised in Britain are
not mentioned here, whence we may suppose that they
are little known on the Continent.

It is here laid down that a good extract of meat should
contain no albumen, and at most 1·5 per cent of fat. It
should not contain more than 21 per cent of water, and
from 56 to 65 per cent of matter soluble in alcohol at 80°.
Its proportion of ash varies between 15 and 25 per cent,
principally sodium chloride and phosphates.

Papaine is inactive in an acid solution, but in an alka-
line solution it digests in a few hours from 70 to 85 times
its weight of meat. Gelatin-peptone, we are reminded,
has scarcely any nutrient value. Some years ago *Les
Mondes* informed us that an artificial peptone was being
manufactured in Paris from a most revolting substance.

A biscuit used, at least experimentally, in the German
army in 1885, is composed of wheat flour, lard, and beef,
grated with a suitable quantity of salt and spices.

Sausages, which may be considered as a form of semi-
preserved meat, seem to have been overlooked by the
author. This is the more to be regretted since they often
contain matter grossly unfit for human food and are in a
dangerous state of decomposition, and require a bacterio-
logical examination. The *hack-fleisch* of the Germans,
which is simply raw sausage-meat without a skin, is one

of the forms in which trichinæ are introduced into the
human system.

The use of borax for the preservation of alimentary
matters is, at least, very questionable, and pending
further inquiry it should be avoided. Its addition to
wines, like that of salicylic acid, is denounced by the
Consultative Committee of Hygiene in France.

We can strongly recommend this volume to hygienists
and medical practitioners.

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*Alkali, &c., Works Regulation Acts,* 1881 *and* 1892.
Thirty-second Annual Report on Alkali, &c., Works.
By the CHIEF INSPECTOR. Proceedings during the
Year 1895 ; presented to the Local Government Board
and to the Secretary for Scotland. Ordered by the
House of Commons to be printed, May 12th, 1896.
Her Majesty's Stationery Office.

MR. A. E. FLETCHER, after ably filling the office of Chief
Inspector for eleven years, has retired, and has been suc-
ceeded by Dr. R. Forbes Carpenter. Dr. A. C. Fryer has
been advanced to the rank of full Inspector, in especial
charge of the South Wales and South-west England dis-
tricts. We have every confidence that the present staff
will continue to work on the lines laid down by their
predecessors.

The number of works now registered in Britain is 1191,
of which 1065 are scheduled as alkali works. Since 1894
there has been a decrease of one alkali work and an in-
crease of ten other works which come under the Acts.

As regards alkali works, frequently so-called, the escape
of hydrochloric acid liberated is slightly over one-third of
the legal standard. In like manner, the average amount
of escape of acid compounds of sulphur and nitrogen is
only 1·158 grain, and less than one-third of the legal
standard, *i.e*, 4 grains calculated as sulphuric anhydride
per cubic foot. The number of prosecutions has been
only 9, all for non-registration.

The total salt decomposed in the alkali process has
been 836,787 tons, a considerable increase. The ammonia-
soda process now, however, takes the lead as to the
quantity of salt decomposed, having consumed 428,614
tons as against 408,173 tons used in the Leblanc method.

Three electrical processes are now coming into opera-
tion, viz., the patents of Messrs. Holland and Richardson,
carried out by the St. Helens Electro-chemical Co. ;
those of Castner and Kellner, being brought into opera-
tion at Weston Point, near Runcorn, by the Castner-
Kellner Alkali Co. ; and the Hargreaves and Bird's
electrolytic process, which has been experimentally worked
at Farnworth, near Widnes.

Full credit is here given to the United Alkali Co. for
their care in keeping their plant in the highest state of
efficiency and in preventing all leakage.

As regards the recovery of sulphur from tank-water
by the Chance-Claus process, no notable improvement is
recorded.

Our old friend the Sankey Brook still emits hydrogen
sulphide into the air of St. Helens, and this renders it
difficult to trace the source of any escape of this gas.

The Oldbury Alkali Co. are still producing cement
from the slurry as it leaves the carbonators, and are con-
fident that they can meet the demands of engineers.

Complaints of the escape of chlorine are now ex-
tremely rare.

The production of superphosphate in this country is
now close upon a million tons, the amount in the United
States being at least equal, that in Germany 600,000, in
France 750,000, Belgium 300,000, Denmark and Holland
200,000, Italy 50,000. The total expenditure on agricul-
tural chemicals is now above £22,000,000.

The production of ammoniacal salts in the United
Kingdom, calculated as sulphate of ammonia, shows a
considerable increase, and means an increase in the
national wealth of more than 1½ millions yearly, obtained

mainly from sources formerly neglected. Among the secondary products of coke, benzol is being recovered to a serious extent.

It must not be forgotten that the production and sale of chemical works have to suffer heavily from the prolonged depression in agriculture,—a calamity for which relief is scarcely conceivable unless our electricians can do away with spring frosts and heavy rains in July and August.

The makers of cement have to contend with low wages paid by their Continental competitors.

Some relief seems obtainable by the disuse of open kilns. A case is quoted where a firm owns two works, one consisting of forty open kilns, whilst the other work is equipped with modern chamber kilns, slurry and clinker grinding-mills, &c. The whole of the work done by this firm during the year has been effected at the modern works, and the forty open kilns have stood idle.

It need scarcely be said that the export trade in cement is practically at an end.

The two great obstacles to the development of British chemical manufactures are the demand for a prohibitive scale of wages, especially in the coal trade, and the examinational system of education, of which not even the recent collapse of China has cured us.

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*The Parallelogram of Forces as Foundation of the Periodic System in Chemistry.* ("Das Parallelogramm der Kräfte als Grundlage des Periodisches Systems in der Chemie.") By Dr. JOACHIM SPERBER. Zurich: E. Speidel. 1896.

THE author recognises the primary unity of all the elements which is demanded by the phenomena of allotropy.

Two points have struck him concerning the periodic system. In the first place, it is from the present point of view quite inconceivable that different quantities of one and the same primitive matter are equivalent; e.g., 1 part by weight of hydrogen, 7 parts of lithium, 22·99 sodium, 39·03 parts of potassium, 85·2 parts of rubidium are equivalent, and an equal quantity of matter is heterovalent; e.g., 35·37 parts by weight of chlorine can be from monovalent to septavalent. This the author holds—and here comes the nucleus of his hypothesis—is only possible if the atoms enter in combination at definite angles, so that the valence indicates only the value of the components which the atom supplies to the resulting compound.

Secondly, it is remarkable, and cannot be accidental, that the physical and chemical properties of the elements are periodical functions of the atomic weights, just as goniometric functions—sine, cosine, tangent, and cotangent—are periodic functions of the angles. In the periodic angular system the minimum of the angle of the equivalents is 70·47 for carbon; the maximum for the monovalent metals, gold, mercury, and thallium, is 89·70; greater angles, from 90° to 270°, would show a negative valence.

An element of the angular equivalence O would have no valence. Its atoms, therefore, would enter into no chemical combination and would oscillate at right angles to the longitudinal vibrations of the mols. of the other elements. This element might possibly be the cosmic ether. Recent researches, we may here add, point to the possible existence of such elements.

We find the remark that, from the point of view of the periodic angular system, the theory of a constant valence of the elements seems completely erroneous. The valence of an element depends on the angle at which it enters into combination. This angle can be modified by external agencies, pressure, temperature, electricity, light, &c.

The remainder of this pamphlet can be fully and fairly judged only by eminent mathematicians. We cannot help regretting that Dr. Sperber has not seen his way to a statement of his theories in plain language, reserving mathematical developments for some future occasion. We find him (p. 26) referring to Boltzmann as having " in a mathematical way, in which a chemist can scarcely follow without dizziness." calculated the dissociation heat of iodine as 14·265 cal., whilst our author makes it as much as 21·0 cal.! Respecting the hope that Dr. Sperber will be able to expound his theory in a form intelligible to chemists, we are of opinion that he has come upon truth which merely wants to be disentangled.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxii., No. 23, June 8, 1896.

**Study of Cast Vanadium and of Vanadium Carbide.**— Henri Moissan. — This memoir will be inserted in full.

**On a New Method of Preparing Alloys.**— Henri Moissan.—The method of preparation indicated in the author's former paper for the alloy of aluminium-vanadium, by setting out from vanadium, is applicable to a number of oxides, and is founded on the powerful affinity of aluminium for oxygen. By this method I have been able to obtain alloys of aluminium with the majority of refractory metals which I had isolated by reduction in the electric furnace. The process consists in throwing into a bath of liquid aluminium a mixture of the oxide to be reduced and of aluminium filings. The preparation is effected in the dry way, and without the addition of any flux. I have thus obtained alloys of aluminium with nickel, molybdenum, tungsten, uranium, and titanium. We consider that this method is general, and will permit us to obtain a number of new alloys.

**Nature of the Chemical Process which Governs the Transformation of the Potential from which the Muscles derive the Energy necessary for Work.**—A. Chauveau. — The author's researches have been made from a perfectly general point of view. They form part of a total from which they have been withdrawn for the demonstration of the law of equivalence in the transformation of force in animals after a comparison of the positive and the negative work of the muscles.

**Spectra of the Non-Metals in Melted Salts.**—A. de Gramont.—This paper will be inserted in full.

**Contribution to the Study of Capillary Affinities.**—M. Lachaud.—The author examines some of the properties of animal charcoal, such as its hygrometric character, its action upon solutions, its behaviour with a mixture, the *rôle* of its porosity, the influence of molecular weight in a series, and a comparison of various blacks among themselves.

**Determination of Potassa.** — Charles Fabre. — This paper will be inserted in full.

**Evaporation Heat of Formic Acid.**—Miss Dorothy Marshall. — This research has been executed in Prof. Ramsay's laboratory at University College.

**Combination of Antipyrine with the Oxybenzoic Acids and their Derivatives.**—G. Patein and E. Dufau.—The authors examine the action of antipyrine with sodium salicylate, with methyl salicylate, with anisic acid, and with saligenine.

**Composition of the Red Pigment of Amanita muscaria.**—Dr. A. B. Griffiths.—This pigment has the composition $C_{19}H_{18}O_6$. It is insoluble in water, but

soluble in chloroform and ether. Its solutions do not give in the spectroscope characteristic absorption bands.

**On Lighting with Acetylene.** — G. Trouvé. — This paper requires the three accompanying figures.

### No. 24, June 15, 1896.

**The Variations observed in the Composition of Apatites.** — Adolphe Carnot. — The crystalline calcium phosphates contain a uniform proportion of calcium fluoride or chloride, so that the composition is—

$$P_2O_5.3CaO + \tfrac{1}{3}Ca(F.Cl)_2,$$
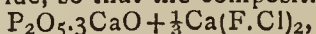
or, in the unitary notation, $Ca_5P_3O_{12}(F.Cl)$. It is remarkable that the only instance known of a tribasic calcium phosphate free from the normal proportion of calcium fluoride, chloride, and even carbonate, is deprived of any external crystalline form, although it presents the cleavage and the optical properties of a true apatite.

**Alimentary Value of Bread made from Flours sifted to different Degrees.** — Aimé Girard. — Really useful bread, which man ought to prefer if careful of his health or of his pocket, is made from flour sifted to the degree of 60, 65, and even 70 per cent. The rule for a truly economical use of the grain of wheat is to reserve at most 70 per cent for human consumption in the form of bread, and at least 30 per cent for feeding cattle. What man does not take in the form of bread, he recovers in the state of meat.

**Dissociation-Spectra of Melted Salts. Alkaline Metals: Sodium, Potassium, Lithium.**—A. de Gramont.—In studying the line-spectra of the non-metals in salts melted by means of the spark strongly concentrated, it is advantageous to make use of the salts of the alkaline metals, on account of the simplicity of their spectra. We need merely deduct from the entire spectrum a small number of known rays to have those of the non-metal in question. In this dissociation of their melted salts the spectra of the alkaline metals differ from those hitherto described. Many of the lines become extended and diffused, others almost disappear. Practically, and especially in presence of the non-metals, the spectrum of sodium is reduced to three bright characteristic double rays,—Na $\delta$, Na $\alpha$ (Frauenhofer D), Na $\beta$, each blended into a single ray in a more prismatic apparatus. In potassium, the classical red rays, K $\delta$, situate at the extremity of the spectrum, are always very diffuse. The K $\gamma$, is very bright and characteristic. There are also, in the red, three very distinct rays :—630·8, 624·55, 611·75. The brightest group is K $\alpha$, in the green, which gives the most sensitive reaction in the scale. Lithium has six rays, easily seen and very characteristic :—670·6, strong and bright ; 610·3, very strong ; 497·2, strong ; 460·3, strong, broad, diffused ; 427·3, readily seen ; 413·2, readily visible, but very diffuse.

**A Reaction of the Cuprous Compounds which may serve to Characterise the Nitrites.**—Paul Sabatier.— (See p. 6).

**On the Zircono-tungstic Compounds.** — L. A. Hallopean. — The author describes a zircono-decitungstate $10WO_3, ZrO_2 4K_2O + 15H_2O$ ; the dizircono-decitungstate, $10WO_3, 2ZrO_2 4K_2O + 20H_2O$ ; and the ammonium zircono-decitungstate, $10WO_3, 5(NH_4)_2O + 11H_2O$.

**Synthesis of Natural Methyl-heptenone.** — Ph. Barbier and L. Bouveault.—Not suitable for abridgment.

**Action of the Porcelain Filter upon the Poison of the Viper: Separation of the Toxic Substances from those which act as Vaccines.** — C. Phisalix. — In the venom of the viper the " vaccinating " substances are distinct from the toxic matters, and may be separated by filtration (apparently with the Chamberland filter).

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*Bulletin de la Société Chimique de Paris.*
Series 3, Vols. xiii.-xiv., No. 23.

**Preparation of Methyl Nitrate.** — M. Delépine. — The author adopts a modification of the Champion process. He uses nitric acid of 36° instead of 48°, and adds at the conclusion sulphuric acid, which causes an almost instantaneous separation of the ether.

**Nitro-Substitutions.** — C. Matignon and M. Deligny. —The isomers of position have the same combustion-heats, excepting experimental arrows. In thermic researches it is sufficient to operate upon one of the three terms—the ortho, meta, or para. The differences oscillate around 45 calories, and are almost independent of the function of the substance in which substitution is effected. The generating equation of these ratio-compounds, deduced from the mean value of 45 cals., leads to a thermic liberation of 36·7 cals.

**Condensation-products of Isobutyric Aldehyd.**— G. Urbain.—It results from the reaction obtained that the isomer of dimethyl hexanalone has really the constitution which theory leads us to expect. The second part of this investigation gives the mechanism of the action (studied by Fossak) of concentrated alcoholic potassa upon isobutyric aldehyd.

**Fission of Dioxystearic Acid.**—P. Freundler.—It is certain that dioxystearic acid obtained by setting out from oleic acid is a racemic acid, a fact quite in accord with the theory of Guye. In dioxystearic acid two of the masses are very heavy, and must attract the centre of gravity of the tetrahedron towards the edge which connects them, and consequently towards the primitive plane of symmetry.

**Certain Chlorated Ethers.**—P. Freundler.—This extensive memoir does not admit of useful abstraction.

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*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 5, Vol. i., No. 3.

**Report presented in the name of the Committee of Chemical Arts on the Labours of M. Effront.**—The authors explain the results which M. Effront has obtained by introducing fluorides into the industries of fermentation.

**Manufacture of Linoleum.**—Walter F. Reid.—From the *Journal of the Chemical Society*.

**Part Played by Alumina in the Production of Glass.**—From the *Comptes Rendus*.

### No. 4.

**Report presented on behalf of the Committee of Economical Arts, by M. Violle, concerning a System of Gas-Bnrners devised by A. Bondsept.**—The principle of the system consists in mixing intimately the coal-gas with air, at the very extremity of the burner. It is said to increase both the yield and the brilliancy of the Auer burner ; but the manner in which this is supposed to be effected requires for its explanation the twenty-three accompanying figures.

**Determination of the Essential Oils by means of Common Salt.** — M. Kutscheroff.—This bulky memoir cannot be intelligibly reproduced without the five illustrations and the numerous accompanying tables.

**Mechanical and Thermic Properties of certain New Glasses devised by Winkelmann and Schott, summarised by H. Le Chatelier.**—The reporter holds that boric acid and zinc oxide, ingredients required in the glasses of the inventor, are not miscible in the proportions indicated.

**Refuse Destructors.** — Stevenson Macadam. — From the *Journal of the Chemical Society*.

**A New Derivative of Cellulose.** — Clayton Beadle and Arthur Little.—Apparently from the *Journal of the Franklin Institute*.

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*Revue Universelle des Mines et de la Metallurgie.*
Series 3, Vol. xxxiv., No. 1.

This number contains no chemical matter.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1911.

## RESEARCHES ON THE METALLIC CARBIDES.*

### By HENRI MOISSAN, Membre de l'Institut.

DEFINITE and crystalline combinations of carbon with metalloids and metals have as yet been very little known. It is only known that certain metals, such as iron, can dissolve carbon, giving rise to " cast " metals (*fontes*).

The knowledge that chemists possess on this point is the slighter inasmuch as these combinations are only produced at a very high temperature. The use I have made of the electric arc as a means of heating in the laboratory has enabled me to examine this question. In the present note I will give an account of my researches on this subject.

At the high temperature of the electric furnace certain metals, such as gold, bismuth, lead, and tin, do not dissolve carbon.

Liquid copper only takes up a very small quantity, sufficient, however, to change its properties and profoundly modify its malleability.

Silver at its boiling-point dissolves a small quantity of carbon, which it gives up on cooling in the form of graphite. This cast silver, obtained at a very high temperature, possesses the curious property of increasing in volume when passing from the liquid to the solid state. This phenomenon is analogous to what is met with in iron. Silver and pure iron diminish in volume when passing from the liquid to the solid state; on the other hand, cast iron and cast silver under the same circumstances increase in volume.

Aluminium possesses identical properties.

The metals of the platinum group at their temperatures of ebullition dissolve carbon with facility, and abandon it in the form of graphite before they solidify. This graphite is abundant.

A large number of metals, on the other hand, at the temperature of the electric furnace produce definite crystalline compounds.

In 1836 Ed. Davy showed that potassium could unite with carbon and produce a compound decomposed by water with evolution of a new hydrocarbon. It was thus that this *savant* discovered acetylene, the synthesis of which was later on effected by M. Berthelot.

On heating a mixture of lithia or carbonate of lithia and carbon in my electric furnace, I have obtained with facility carbide of lithium in transparent crystals, disengaging per kilogrm. 487 litres of pure acetylene gas,—

$$C_2Li_2 + H_2O = 2LiOH + C_2H_2.$$
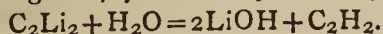
In the same way, by heating in my electric furnace a mixture of an oxide and carbon, I have been the first to obtain by a general method, in the pure crystalline state, and in notable quantities, the carbides of calcium, barium, and strontium. The carbide of calcium had already been prepared in the form of a powder, black, amorphous, and impure. Without going into the history of the subject, I may recall the researches of Wöhler, of M. Maquenne, and those of M. Travers on this subject.

All these carbides are decomposed on contact with pure water with disengagement of acetylene. The three alkaline-earthy carbides have a formula corresponding to $C_2R$, and carbonate of lithium to the formula $C_2Li_2$. The industrial preparation of acetylene is founded on this reaction.

Another type of carbide, crystallising in hexagonal plates, transparent, and of a centimetre in diameter, is

furnished by aluminium. This metal strongly heated in the electric furnace in the presence of carbon is filled with yellow plates of carbide, which may be isolated by a sufficiently delicate treatment, by means of a weak solution of hydrochloric acid cooled to the temperature of melting ice. This metallic carbide is decomposed by water at the ordinary temperature, furnishing alumina and pure methane gas. It has the formula—

$$C_3Al_4 + 12H_2O = 3CH_4 + 2(Al_2(OH)_6).$$
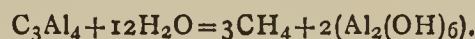
My assistant, H. Lebeau, has obtained under the same conditions carbonate of glucina, which also furnishes, in cold water, pure methane.

The metals of the cerite group have given us crystalline carbides, the formula of which is similar to that of the alkaline-earthy carbides, $C_2R$. We have specially studied the decomposition by water of the carbides of cerium, $C_2Ce$, of lanthanum, $C_2La$, of yttrium, $C_2Y$, and of thorium, $C_2Th$. All these bodies decompose water, yielding a gaseous mixture rich in acetylene and containing methane. With the carbide of thorium the acetylene diminishes and the methane increases.

None of our experiments with iron have given us definite crystalline compounds. At the ordinary pressure and at a high temperature iron has never furnished a definite compound.

It has long been known, thanks to the researches of MM. Troost and Hautefeuille, that manganese gives a carbide, $CMn_3$. This carbide may be prepared with the greatest ease in the electric furnace, and in contact with cold water it yields a mixture of equal volumes of methane and hydrogen,—

$$CMn_2 + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$
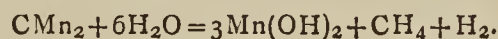
Carbide of uranium, $C_3Ur_2$, which I have obtained by the same methods, gives a more complex reaction; the carbide, well crystallised and transparent when in thin pieces, is decomposed in contact with water, yielding a gaseous mixture containing a large quantity of methane, of hydrogen, and of ethylene. But the most interesting fact about this carbide is the following :—The action of cold water not only produces gaseous hydrocarbons,—it forms in abundance liquid and solid hydrocarbons. Two-thirds of the carbon in this compound is recovered in this form.

The carbides of cerium and lanthanum, by their decomposition in water, have also furnished us with liquid and solid hydrocarbons, but in small quantity.

All these carbides, decomposable by water, at the ordinary temperature, with production of carburetted hydrogens, constitute the first class of compounds of the family of metallic carbides.

The second class is furnished by the carbides which do not decompose water at the ordinary temperature, such as the carbides of molybdenum, $CMo_2$, of tungsten, $CW_2$, of chromium, $CCr_4$ and $C_2Cr_3$. These latter compounds are crystalline and non-transparent, with metallic lustre. They possess great hardness, and only fuse at a very high temperature. We have prepared them all in the electric furnace, and have given the detail of the experiments, together with all the analyses, in the *Comptes Rendus de l'Académie des Sciences de Paris*.

The metalloids have also furnished with carbon, at the temperature of the electric furnace, crystalline and definite compounds. We may mention, for example, the carbide of silicon, $CSi$, discovered by Mr. Acheson, and prepared to-day in commerce under the name of carborundum; the carbide of titanium, $CTi$, the hardness of which is sufficient to scratch diamond; the carbide of zirconium, $CZr$; and the carbide of vanadium, $CVa$. We have described the preparation and properties of these new carbides.

One general fact is noticeable in the numerous researches which I have undertaken with the electric furnace :—The compounds produced at a high temperature have always a very simple formula, and most frequently

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* A Paper read before the Royal Society.

there only exists one combination. But the most curious reaction brought to light in these researches is the easy production of hydrocarbons, gaseous, liquid, or solid, by the action of cold water on certain of these metallic carbides. It seems to us that these studies should have a certain interest for geologists. The disengagement of more or less pure methane which is met with in certain localities, lasting for ages, may have its origin in the action of water on carbide of aluminium.

Starting from 4 kilogrms. of carbide of uranium, we obtained in one experiment more than 100 grms. of liquid hydrocarbons. The mixture thus obtained is composed in great part of non-saturated ethylenic carbides, and a small quantity of acetylenic carbides. These carbides are produced in the presence of a large proportion of methane and hydrogen at the atmospheric pressure and ordinary temperature: this leads us to think that when the decomposition takes place at an elevated temperature there will be produced saturated hydrocarbons analogous to petroleums. M. Berthelot has, in fact, established that the direct fixation of hydrogen on a non-saturated hydrocarbon may be effected by the sole action of heat.

The existence of these new carbides destructible by water may therefore modify the theoretical ideas which have been hitherto advanced to explain the formation of certain petroleums or other carbonaceous products. It is very certain that we must guard ourselves against too hasty generalisations. It is probable that there exist petroleums of different origins. At Autun, for instance, the bituminous schists certainly appear to have been formed by the decomposition of organic matters. On the other hand, in the Limagne, the asphalte impregnates all the fissures of an Aquitanian limestone which is very poor in fossils. This asphalte is in direct relation with the veins of peperite (basaltic tufa), and consequently in evident relation with the volcanic eruptions of the Limagne.

A boring recently made at Riom, at 1200 metres depth, led to the flow of several litres of petroleum. The formation of this liquid hydrocarbon in this locality may be attributed to the action of water on metallic carbides.

In connection with carbide of calcium we have shown that under some conditions this compound may burn and give rise to carbonic acid. It is probable that, in the earliest geologic times, nearly all the carbon on the earth existed in the form of metallic carbides. When water intervened in the reactions the metallic carbides have given rise to hydrocarbons, and, by oxidation, to carbonic acid. We may find an example of this reaction in the environs of St. Nectaire. The granites which in this place form the edge of the tertiary basin give off continuously, and in great quantity, carbonic acid gas.

We also think that certain volcanic phenomena may be attributed to the action of water on easily decomposable metallic carbides. All geologists know that the last manifestation from a volcanic centre consists of very varied carbonaceous emanations, ranging from asphalte and petroleum to the ultimate term of all oxidation, carbonic acid.

A movement of the earth causing the contact of water and metallic carbides may produce a violent disengagement of gaseous masses. As the temperature rises the phenomena of polymerisation of the carbides intervene to furnish a long series of complex products. The hydrocarbons may thus be at first formed. The phenomena of oxidation appear to follow and complicate the reactions. In certain places a volcanic fissure may act as a powerful draught chimney. It is known that the nature of the gas collected in the fumerolles varies according as the volcanic centre is immersed in the ocean or surrounded with atmospheric air. At Santorin, for instance, M. Fouqué has collected free hydrogen in the submerged volcanic vents, while in the land fissures he only detected aqueous vapour.

The existence of these metallic carbides, so easy to prepare at high temperatures, and which may probably be encountered in the deeper strata of the globe,* enable us therefore to explain in some cases the formation of liquid or solid hydrocarbons, and the cause of certain volcanic eruptions.

## THE ESTIMATION OF NICKEL IN STEEL, &c.

### By H. BREARLEY.

THE well known instructions for separating iron from manganese, nickel, &c., by precipitating with sodium or ammonium acetate are :—Solution must be neutral, with slight turbidity, or solution must have only a few drops of acid in excess.

In separating Ni in this way it was noticed that if, after clearing up the slight turbidity with HCl, the addition of acid was continued, the browny red colour disappeared, and the solution had the lemon colour usually possessed by iron solutions when much free HCl is present. I was surprised to find that with this somewhat large excess of free acid the iron could be precipitated by ammonium or sodium acetate; and, moreover, the percentage of Ni separated in one precipitation was greater than could be obtained with ordinary neutralisations. Even beyond this straw colour, as much as 1 c.c. strong HCl could be added when operating on 500 c.c. of solution, and under such circumstances the Ni separation was almost complete in one precipitation. With so large an excess of free acid, the ferric acetate readily re-dissolved as the solution cooled, and the results obtained were not strictly uniform unless 2 or 3 c.c. of acetic acid were also present. This led me to see if a large excess of acetic acid with only a slight excess of HCl would give satisfactory results. It turned out to be better than the HCl, and I found that as much as 100 c.c. strong acetic acid could be added before the acetate precipitation when operating on 1 litre of solution ; 50 c.c., however, will give an absolute separation of Ni and Fe.

These facts may have been previously noticed. They were, however, unknown to me, and no book on steel analysis I am acquainted with (" Select Methods," Blair, Arnold, &c.) gives instructions very dissimilar to those noted at the beginning of this article.

The method based on these facts is as follows :—

Weigh 1 grm. of steel into an 1100 c.c. beaker, dissolve in 20 c.c. $HNO_3$ (1·20), cool somewhat; add dilute ammonia to slight precipitation, and then HCl until it quite disappears; add 70 c.c. strong acetic acid, hot water to 950 c.c. or so, 50 or 70 c.c. ammonium acetate, and boil. Make up to 1000 c.c., and filter off one-half the solution. Transfer to a large flask and cool, make faintly but distinctly alkaline with ammonia, add 2 c.c. KI and 2 c.c. $AgNO_3$. Iodide of silver is formed in the solution ; now run in standard potassium cyanide until the AgI dissolves, and the solution is as crystal clear as it was before the silver nitrate was added.

The KCN is standardised as follows (since it alters its strength from week to week it should be standardised every few days) :—

To the clear solution of the titrated sample 10 or 20 c.c. of standard Ni is added and titrated with KCN. We thus know the value of 1 c.c. KCN in terms of nickel. Several indicators are now added to the clear solution and titrated, and thus the KCN necessary to dissolve one AgI indicator is found. The necessary calculations need no further explanation. It is better to standardise on the sample solution, so that the KCN may be measured under identical conditions in each case.

Here are some results on ordinary steel to which definite quantities of the standard nickel had been added :—

* The difference between the mean density of the earth and that of its superficial crust appears to point to the existence of a central mass rich in metal. The existence of metallic iron meteorites strengthens this hypothesis.

| Nickel added. Per cent. | Nickel found. 70 c.c. acetic. | 100 c.c. acetic used. |
|---|---|---|
| 1 | 1·003 | 1·003 |
| 2 | 1·990 | 1·988 |
| 3 | 3·000 | — |
| 4 | 3·992 | 4·014 |
| 5 | 4·996 | 5·004 |

A sample of steel sent from the works gave 5·1 per cent nickel. We were subsequently informed that the sample had been most carefully prepared, and the maximum theoretically present was 5·146 per cent.

The accuracy of the method is undoubted, and when a number of estimations are to be made the time required does not exceed thirty minutes. I propose to note a few points which greatly enhance the rapidity of the estimation, and to show that they introduce no inaccuracy.

*Hot Water for Filling up.*—Many books state that the solution must be cold before the acetate is added. This is probably because the iron comes down at a low temperature when no excess of acid is present. With 70 to 100 c.c. free acetic acid, the precipitate does not appear before 85—90° C. If the precipitation occurs immediately on the addition of acetate the results are low; e.g., boiling water was added to two samples containing 3 per cent Ni, precipitation followed almost instantaneously, and the results were 2·92 and 2·91 per cent; but two other samples which came down on heating for one to two minutes gave 3·01 to 3·00 per cent.

*Filtration.*—At first I filtered through fluted English papers. It was always necessary to filter until the pores of the paper had become stopped somewhat, and during this time the solution was getting cold, and not unfrequently re-dissolving some of the ferric acetate, as it will do if the temperature falls below the point of formation. The time required was from 5 to 10 minutes. I now use a funnel whose stem is horizontal at the tip, place a perforated plate (1½ inches diameter) therein, and cover with a layer of fibrous asbestos, such as is used for filtering carbons and used with the Gooch crucible. The under side of the plate and the stem of the funnel must be filled with water. After the solution is made up to 1000 c.c. it is returned to the beaker and kept well wrapped in dusters. In ten or fifteen minutes nearly all the iron has settled. About 60 c.c. is poured on to the asbestos and allowed to run through. This is repeated until about 300 c.c. is passed; by this means the water is completely driven from the asbestos and stem. The next 500 c.c. is collected for titration. The total filtration does not take more than a minute. That the above method of filtration introduces no inaccuracies may be readily seen by supposing each 60 c.c. mixes with the water in funnel, for instance. A filter made with strong HCl in this way gave only a slight opalescence with silver nitrate after the passage of the last 60 c.c.

### Influence of Special Elements.

*Tungsten* may be separated by solution in aqua regia, evaporating to dryness, filtering off $WoO_3$, and proceeding with filtrate as usual; but it occasions little difficulty to proceed as though no W was present.

*Manganese.*—The Mn is separated along with the Ni; it exerts no influence on the titration, as may be seen:—

| | Mn present. | | Ni found. | |
|---|---|---|---|---|
| | 1·65 p.c. | 20·03 p.c. | 1·65 p.c. | 20·03 p.c. |
| Ni added | nil | nil | nil | nil |
| „ „ | 2 p.c. | 2 p.c. | 2 p.c. | 2·008 p.c. |

*Chromium* gives to the filtrate a pinky colouration; this turns light brown when the solution is made alkaline, and though no precipitate appears, the slight opalescence towards the end of the reaction is more easily overlooked than in a colourless solution. If the iron precipitate is boiled for half an hour the filtrate is colourless, and the filtration occasions no difficulty.

*Copper* cannot be separated by means of lead, zinc, aluminium, &c., without in turn needing to be separated themselves, because they react in the final titration. It may be precipitated by means of $H_2S$ or sodium hyposulphite in an acid solution just after dissolving. A more expeditious way, however, is to proceed as usual, and then to the filtrate containing Ni and Cu add excess of $H_2SO_3$ and 5 c.c. KCNS, 2 per cent solution (Crookes, "Select Methods," 3rd ed., p. 294). Slightly better results are obtained by adding 25 c.c. dilute ammonia (3 to 1) to neutralise about half the free acid. The precipitated subsulphocyanide is filtered through asbestos. The precipitate has a tendency to run through on washing; it is therefore advisable to measure the quantity filtered through and measure the quantity retained in the funnel stem and asbestos, and make the necessary correction, always remembering that the nickel solution in the funnel has displaced an equal volume of water with which the asbestos filter was made. The excess of $H_2SO_3$ affects the titration but very slightly, if at all; but if pure KCNS is not obtainable, a blank estimation should be made. Some estimations made in this manner gave:—

| Cu added. Per cent. | Ni added. Per cent. | Ni recovered. |
|---|---|---|
| 1 | 2 | 1·981 |
| 1 | 2 | 1·978 |
| 3 | 2 | 1·968 |
| *2 | 2 | 1·970 |

* Was made with KCNS containing KCN.

### Particulars of Reagents.

*Ammonium Acetate.*—Made by neutralising acetic acid with ammonia. Approximately 580 c.c. acetic acid and 180 c.c. ammonia.

*Potassium Cyanide.*—4½ grms. per litre.

*Standard Nickel.*—Cube nickel contains about 99·5 per cent pure nickel. So much as equals 1 grm. pure nickel is dissolved in small quantity of nitric acid and made up to 1 litre. If the Ni contains much iron it should be separated with ammonium acetate, &c.

*Silver Nitrate.*—2·5 grms. per litre.

*Potassium Iodide.*—20 grms. per litre.

Preliminary experiments have been made with a view of separating other metals from iron in this way. I hope to report progress shortly.

The Laboratory, Norfolk Works, Sheffield.

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## ARSENATE OF LEAD, A NEW INSECTICIDE.*

### By FRANK T. SHUTT, M.A., F.I.C., F.C.S.

THIS substance has been recommended as a substitute for Paris green in spraying mixtures used for the destruction of "biting" insects, such as the apple worm (Codling Moth) and the Plum Curculio. Being insoluble in water, and reported as non-injurious to foliage, it is held that it may with safety be employed in larger amounts than those given in the formulæ containing Paris green; at the same time it is said that this compound is equally as efficacious in the extermination of insect foes as the latter well-known and widely used insecticide.

Since many erroneous and misleading formulæ have appeared in print for its preparation, it has been thought advisable to ascertain the exact chemical nature of the compound used, and to deduce therefrom the correct weight of the materials to employ, corroborating the latter by actual experiment. It is probable that some of the apparent discrepancies in the published formulæ have been due to the employment of crude and impure arsenate of soda, such as is used in calico-printing. The chemi-

* From the "Report on Experimental Farms to the Department of Agriculture, Canada."

cals used are acetate of lead and arsenate of soda, the result of the reaction on mixing solutions of these being the formation of an insoluble precipitate of lead arsenate, acetate of soda remaining in solution. Lead arsenate so formed is a white amorphous compound, settling to the bottom of the vessel on standing. The reaction when using pure reagents is represented by the following equation :—

$$2Na_2HAsO_4,7H_2O + 3Pb(C_2H_3O_2)_2 = Pb_3(AsO_4)_2 +$$
(Arsenate of soda).   (Lead acetate).   (Lead arsenate).

$$+ 4NaC_2H_3O_2 + 2HC_2H_3O_2 + 14H_2O.$$
(Acetate of soda).   (Acetic acid).   (Water).
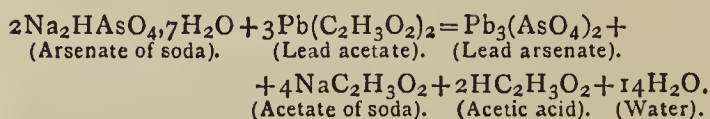
### Directions for Preparing the Insecticide.

To prepare fifty gallons of the mixture at the rate of one pound of lead arsenate to 200 gallons of water :—Dissolve 3 ounces of arsenate of soda in a quart or so of water (it dissolves readily in cold water). Dissolve 4¾ ounces of lead acetate in a similar volume of water. Pour both solutions into a barrel already containing about 45 gallons of water and stir well. The volume may now be made up to fifty gallons. This formula provides for the presence of a slight excess of lead acetate in solution ; if the arsenate of soda were in excess, injury would probably result to the foliage.

The lead arsenate remains longer in suspension when precipitated in a large volume of water than when made concentrated and subsequently diluted.

On filtering off a little of the liquid and adding to it a few drops of the arsenate of soda solution (which is reserved for this purpose), a white precipitate should form, showing excess of lead.

It should be remembered that arsenate of soda and acetate of lead, as well as the product, are poisonous.

Respecting the price of the material, I could not obtain any Canadian quotations for commercial arsenate of soda ; the pure article costs about $2 per pound. Acetate of lead retails at 25 cents per pound, or in quantities of five pounds or more at 15 cents per pound. At these prices, the cost of the material for 50 gallons of the insecticide (strength as above) would be about 42 cents.

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## THE REDUCTION OF COPPER SULPHIDE.

### By DELIA STICKNEY.

J. UHL, in his paper " Ueber Einwirkung von Schwefeldioxyd auf Metalle " (*Ber. d. chem. Ges.*, xxiii,, 1215), speaks of reducing copper sulphide by heating it in a stream of hydrogen. A simpler way to accomplish the reduction is to let the compound come in contact with the flame of the ordinary Bunsen burner until a change in colour is seen. Copper sulphide, made by heating copper turnings and flowers of sulphur in an ignition-tube, was held by forceps in the flame for five or ten minutes. The bluish-black sulphide turned dark red, and the odour of sulphur dioxide was noticed. To determine whether this was metallic copper or cuprous oxide, the experiment was made on a larger scale. Copper sulphide, prepared in the usual way, was ground, and heated in a porcelain dish with the flame playing directly upon it. During the heating, the mass showed blue, green, and black colours, shades of red and of metallic copper, and under the lens many threads of bright copper were distinctly seen in the soft spongy mass. The unreduced part was hard and brittle, but the coloured parts were soft and friable. After successive grindings and heatings, very few hard lumps remained, but each time the mass felt softer under the pestle, and looked more like spongy copper.

To see if cuprous oxide was formed in any great amount, equal quantities of this product and of cuprous oxide were treated with concentrated hydrochloric acid ; cuprous oxide dissolved entirely, but the other left a bright residue in the bottom of the tube. A test with ammonia showed

that but little had dissolved. The residue was taken out, dried upon filter paper, and examined under a lens. The greater part was bright copper, but there were also some particles of a dark colour, probably a little of the sulphide not reduced. Some of the product obtained by grinding and heating in this way was put into the flame of the blast lamp, and heated gradually until the copper melted. A little matte, tarnished on the outside, was formed in the bottom of the dish, which analysis showed to contain 97—98 per cent pure copper.

Experiments were now made with copper sulphide heated under different conditions. It was used just as it came from the tube, and heated undisturbed for one to four hours. The hard black mass gradually fell apart loosely, and formed the most beautiful product that had been obtained. Varying shades of red were seen, mixed with iridescent, bluish-black parts, arranged often in bands, and in the centre, and on the bottom, the little bright sheafs of metallic copper containing threads one-fourth to one-half inch in length were very abundant. To see if greater heat hastened the process, the sulphide was heated in the same way by the blast lamp. It melted a little on the edges, but remained a hard, brittle, grey mass with but little of the red colour on it, showing that the gentle reducing action of the Bunsen flame was needed rather than a high degree of heat.

Once the sulphide came from the tube in which it was made so hot that the free sulphur burned in the air. When the action was over, a few red spots were seen here and there. This suggested that a little free sulphur might hasten the reduction, and when the process was half completed, the addition of this seemed to shorten the time. Cupric oxide and cuprous oxide were intimately mixed with sulphur and heated, and here the reduction to copper was much quicker than in the case of the sulphide.

For the purpose of determining if contact with the flame was essential, some of the sulphide was heated for four to five hours in a porcelain crucible with the flame underneath, free contact with the air being allowed. Hardly any change in colour was seen. On the top was a slight reddish tinge, and a little sulphur was set free, but the mass was still hard and dark, keeping its shape. The form of the sulphide seemed to make no difference, for the results were the same whether it was powdered or in the form of filings or foil.

This easy method of reduction may be of use in general chemistry, as forming the complementary part of the familiar experiment with copper and sulphur, illustrating synthesis. The pupils' questions show always the desire to reverse the process, and get the copper back again.—*American Chemical Journal*, vol. xviii., No. 6.

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## THE CONDUCTIVITY OF SOLUTIONS OF ACETYLENE IN WATER.

### By HARRY C. JONES and CHARLES R. ALLEN.[*]

KEISER (*Am. Chem. Journ.*, xiv., 285 ; and xv., 535) has shown by his work on the metallic compounds of acetylene, that both the hydrogen atoms possess acid properties, being capable of substitution by some metals. The compounds of silver and copper are formed by the substitution of two univalent metallic atoms for the two hydrogen atoms in the acetylene, and have the composition indicated by the formulæ $Ag_2C_2$ and $Cu_2C_2$ respectively. In these cases the acetylene conducts itself like a weak dibasic acid.

As the behaviour of acetylene in forming these compounds is that of an acid, it might be expected that it would exhibit, at least to some extent, the conductivity

[*] Solutions were prepared by Jones; the conductivity measurements were made by Allen.

phenomena shown by that class of substances. It appeared, therefore, that the investigation of the molecular conductivity of acetylene might be of interest.

For the cuprous acetylide, from which the acetylene was obtained, we are indebted to Prof. Keiser. The acetylene was liberated from the cuprous acetylide by heating it in a flask, on the water-bath, with a solution of potassium cyanide, as directed by Keiser. The gas was passed into water, which had been re-distilled from acid and alkaline potassium permanganate and condensed in a tube of block tin. The conductivity of the water used was determined and found to be negligible. This solution was tested for cyanogen, which might have passed over in some way, by boiling a portion of it with an alkali and ferrous sulphate, neutralising the alkali with an acid, and adding a ferric salt. No trace of a blue colour was obtained. The usual tests for copper, with ammonia or ammonium sulphide, also gave negative results, thus showing the absence of all possible impurities. Solutions of acetylene thus prepared and tested were used in the conductivity determinations.

Soon after the work was begun it was found that the solutions gave off the acetylene gas very rapidly, even in glass-stoppered bottles, and at temperatures only a little above zero. It was impossible to retain even dilute solutions at a constant concentration for any considerable time. After a number of trials, the following method was adopted as introducing the least error. The thermostat bath of the Kohlrausch-Ostwald conductivity apparatus was replaced by a vessel containing much finely-powdered ice and a little water, giving a temperature which was approximately zero. The acetylene solution of unknown concentration was cooled nearly to zero by placing it in a glass-stoppered bottle and immersing the bottle in a freezing mixture. A portion of this solution was then poured into the resistance cell (which was already in the ice-bath described above), and the position of equilibrium on the bridge determined as rapidly as possible. A known volume of the solution in the cell was then at once drawn off in a pipette, and the amount of acetylene present determined as follows:—A standard tenth-normal solution of silver nitrate and an exactly equivalent solution of potassium chloride were used. The gas was brought into combination by running in an excess of the silver nitrate solution. An equal volume of the potassium chloride solution was then run in, a few drops of a solution of potassium chromate, serving as an indicator, added, and the excess of potassium chloride titrated with the silver nitrate. As there was no loss of acetylene from the solution after the first addition of silver nitrate, the only loss of gas affecting the results was that which took place during the interval between the conductivity measurement and the first addition of silver nitrate, which was, on an average, only two or three minutes. Since the solutions of acetylene were very dilute, and the analyses, of necessity, made with a comparatively small volume, the standardisation of the solutions must be regarded as only roughly approximate. The results of the conductivity measurements of the acetylene solutions are given in the following table. The column headed $v$ gives the volume in litres, which contains a one-half grm.-molecular weight of the gas; $\mu v$ are the molecular conductivities at the volumes $v$.

|   | $v$. | $\mu v$. |
|---|---|---|
| 1. | 417 | 29·0 |
| 2. | 833 | 41·0 |
| 3. | 1111 | 50·0 |
| 4. | 2502 | 77·0 |

Although these results are necessarily affected by considerable error, due to the causes indicated above, yet they undoubtedly show that solutions of acetylene in water are somewhat dissociated, and that this dissociation increases with the dilution—results which would be expected from the weakly acid character of the compound.

—*American Chemical Journal*, xviii., No. 5.

## RESEARCHES ON THE RÖNTGEN RAYS.*

By ALFRED M. MAYER.

(Concluded from p. 8).

3. *The Formulæ of Transmission of the Röntgen Rays through Glass, Aluminium, Platinum, Green Tourmaline, and Herapathite.*

THE Röntgen rays, after their transmission through various substances, produce actinism on a photographic plate, and by the degree of this actinism we have attempted to obtain the formula of transmission peculiar to each substance. This action of the X rays is cumulative and evidently is entirely different from the transmission of light and radiant heat where the maximum of transmission is instantly reached and under proper and controllable conditions remains constant and therefore can be accurately measured. But with the X rays the amount of their action on the plate varies directly as the time of their action (see 4), depends on the distance of the sensitive plate from source of radiation, and on the energy of the source. Therefore this method of determining the constants of the formulæ of transmission of the X rays is somewhat arbitrary; but the exact conditions in the determination of the constants having been given, these conditions can readily be obtained by other experimenters. Thus, to have the same conditions as existed in our experiments, one has only to place a pile of crown glass plates 5·5 m.m. thick, at such a distance from the radiant source that on two hours' exposure the X rays will have just not visibly acted on the photographic plate after having traversed the glass. Some assumption has to be made as to the nature of the X rays, otherwise no progress can be made in determining the constants of their formulæ of transmission. We have assumed that they are homogeneous. The formulæ, as determined, hold good till they have conclusively been shown not to be homogeneous, which is very likely to happen in the progress of research on their nature.

The method used owes whatever merit it may have to the use of the wire netting devised by Professor Rood to give accurate indications of the relative permeability of various substances to the X rays. This wire netting he places on the slide covering the sensitive plate, and on the netting he places substances of various thickness. The netting completely screens the X rays, and its image on the negative is the brightest possible to obtain in the given conditions. If a plate of a substance should also entirely screen the X rays, then the image of the netting is invisible in the photograph of this substance, and as plates of substances allow more and more of the X rays to traverse them, the images of the netting in the photographs of these substances are more and more bright. If the image of the netting in the photographs of two substances should be equally bright, then these two plates transmit equal actinic action to the sensitive plate. Thus this ingenious device serves as a very delicate photometer in determining the fact just mentioned.

It occurred to me that the wire netting could also give me data with which to determine the constants of the formulæ of transmission of the X rays through various substances. The method devised is as follows:—On a wire netting with 8 meshes to the inch placed on the slide of the plate holder, are cemented piles of glass discs (each glass about one-tenth m.m. thick); these piles gradually increase in thickness. These piles of glass were exposed to the action of the X rays, so that the photographic plate was 25 c.m. distant from the radiant source. In the apparatus used this distance could be accurately measured. After an exposure of two hours it was found, on developing the plate, that the netting was *just visible* in the photograph of the pile 5·35 m.m. thick, and that it was not visible in

the photograph of the pile 5·5 m.m. thick. In this last case, though the X rays had penetrated to the sensitive film, yet the difference in the screening effect of the netting and of the glass was not visible, because the eye cannot distinguish between the illumination of juxtaposed surfaces which differ in illumination by about $\frac{1}{100}$. Hence, through the last pile of 5·5 m.m. about $\frac{1}{100}$ of the actinic intensity of the incident beam had passed.

Now the formula of transmission of rays through a substance which does not reflect these rays is $I' = Ia^t$. Where $I'$ = the intensity of the transmitted beam; $I$ = the intensity of the incident beam; $a$ = a constant depending on the substance, and $t$ is an exponent of $a$, and $t$ is the thickness of the substance. We have taken one-tenth m.m. as the unit of $t$.

From the conditions of the experiment, $I' = Ia^t = \frac{1}{100}$, and as $t$ is known, $a$ is readily computed. The accuracy of the determination of $a$ depends on the value of the least perceptible difference in illumination that the eye can distinguish in two juxtaposed surfaces. We have adopted $\frac{1}{100}$ as the most probable value.* But suppose that the fraction is not $\frac{1}{100}$, but $\frac{1}{115}$, or $\frac{1}{85}$, then the departure of these fractions from $\frac{1}{100}$ will affect the constant by 4 units in the third decimal place.

These experiments, made in the conditions we have indicated, give for the formula of transmission through the glass used, a crown glass made by Chance and Co.,—

$$I' = I \times 0.92^t.$$

Having this formula as a basis, it is comparatively easy to determine the constants of another substance, by placing the substance on the netting with piles of glass of graded thickness and exposing them to the X rays. We then see what thickness of glass gives the same illumination to the image of the netting as does the known thickness of the substance. Thus, the netting in the photograph of a disc of herapathite 0·9 m.m. thick had the same brightness as in the photograph of a pile of glass 0·69 m.m. thick. By the formula, glass 0·69 m.m. thick transmits 0·5636 of the incident beam, and herapathite of 0·9 m.m. transmits the same. From this we compute that $I' = I \times 0.9382^t$ is the formula for the transmission of the X rays through herapathite, which for $t = 0.69$ gives 0·5636 of transmission.

In the same manner it was found that—

| M.m. | | | | M.m. | |
|---|---|---|---|---|---|
| 2·05 of aluminium transmits the same as | | | | 2·44 of glass. | |
| 0·02 ,, platinum | ,, | ,, | | 2·9 | ,, |
| 2·0 ,, green tourmaline ,, | | ,, | | 2·0 | ,, |
| 0·69 ,, herapathite | ,, | ,, | | 0·9 | ,, |

From these determinations we have computed the formulæ of transmission of these substances.

| | |
|---|---|
| Glass .. .. .. .. | $I' = I \times 0.92^t$ |
| Aluminium .. .. .. | $I' = I \times 0.905^t$ |
| Platinum .. .. .. | $I' = I \times 0.00063^t$ |
| Green tourmaline .. | $I' = I \times 0.92^t$ |
| Herapathite .. .. | $I' = I \times 0.938^t$ |

Taking the amount of transmission through aluminium of one-tenth m.m. and of 1 m.m. as unity, we have, in the following table, the relative transmission through the substances experimented on.

| | $t = \frac{1}{10}$ m.m. | $t = 1$ m.m. |
|---|---|---|
| Aluminium .. .. .. | 1· | 1· |
| Glass .. .. .. .. | 1·016 | 1·180 |
| Green tourmaline .. | 1·016 | 1·180 |
| Herapathite .. .. | 1·036 | 1·435 |
| Platinum .. .. .. | 0·000696 | — |

Platinum 0·06 m.m. thick is practically impervious to the rays from the Crookes tube used, transmitting only 0·005 of incident beam.

* "Photometric Experiments," O. N. Rood (*American Journal of Science*, July, 1870).

This method of determining the transmission of the X rays through various substances may be criticised, because in the experiments I obtain not alone the transmission through the substances placed on the slide of the plate-holder, but at the same time the transmission through the slide itself. If the slide has a measurable transmission, or, screening effect, then its equivalent in thickness of the substances placed on it should be added to them. This criticism, however, is nought, because experiments have shown that if the thickness of a portion of the slide is doubled by placing on it a piece of the material of which it is made, no screening of the X rays by this piece can be detected.

### 4. *The Actinic Effect of the Röntgen Rays varies inversely as the square of the distance of the sensitive plate from the radiant source.*

The slide covering a photographic plate had on it the wire netting, and the plate was exposed for 30 minutes to the X rays at a distance of 10 inches from the radiant source. Another similar plate in the same plate-holder was exposed for two hours at a distance of 20 inches from the radiant source. These distances could be accurately measured in the apparatus used. These plates were taken from the same box and developed side by side in the same tray. Indeed all the conditions were carefully made the same in the two experiments except the distance of plates from the radiant source. On developing the images on the plates they were exactly alike; the image of the netting had the same illumination on each plate, and the density of the films was the same. This experiment shows that the X rays act on a sensitive plate according to the law of the inverse squares.

From this law it follows that the actinic power of the X rays is not sensibly absorbed in traversing the air; also, that these rays are not sensibly diffused by radiation from the molecules of the air they traverse, the air being at ordinary barometric pressures.

These deductions, which necessarily follow from the law of the inverse square, are, however, at variance with the facts observed by Professor Pupin, who states, in *Science* of April 10, 1896: "There was evidently a diffuse scattering of the X rays in their passage through the air." . . . . . . "These experiments prove, beyond all reasonable doubt, that the Röntgen radiance is diffusely scattered through bodies, gases not excepted." These opinions of Professor Pupin are founded on experiments on the action of the X rays on a fluorescent screen, or, rather on a "fluoroscope," not on experiments on their actinic effects. In the latter case I am confident that the X rays act according to the law of the inverse squares, and therefore are not sensibly diffused. In the former case Professor Pupin finds that they are diffused in traversing the air, and very sensibly diffused if I understand aright his paper; but as he does not give any photometric measures, or estimates, of the intensity of the fluorescence in the geometric image of the slit, and outside of this image, one cannot form an opinion of the amount of the diffusion he describes. The facts of diffusion described by Professor Pupin are opposed to those discovered by so distinguished and experienced a physicist as Röntgen, who, in section 10 of his first paper, writes: "I find, using a Weber's photometer, that the intensity of the fluorescent light varies nearly as the inverse squares of the distance between screen and discharge tubes. This result is obtained from three very consistent sets of observations at distances of 100 and 200 m.m. Hence air absorbs the X rays much less than the cathode rays. This result is in complete agreement with the previously described result, that the fluorescence of the screen can be observed at 2 metres distance from the vacuum tube." Röntgen does not mention any diffusion observed by him in these experiments, and it is certain that he would have mentioned the existence of diffusion in experiments made to determine a law of

radiation, and which diffusion necessarily would have invalidated the law of inverse squares.

The radiation from the Crookes tube, used in the experiments described in this paper, came from a calcined shell supported by the anode wire and placed opposite the cathode. The tube was not sensibly heated during the experiments and the actinic power of its radiation remained constant. It was proved by taking a pin-hole photograph of the naked tube, with an exposure of two hours, that by far the larger proportion of the X rays emanated from a 4 m.m. square surface of the shell which was acted on by the cathode rays. The walls of the glass tube, as was proved by other independent photographic experiments, furnished a small percentage of X rays, but not enough to make their presence known in the pin-hole photograph, which had furnished quite a dense image of a portion of the shell. Furthermore the X rays from the glass wall itself were cut off and prevented from reaching the photographic plate by a diaphragm of lead with a circular opening of one-half inch, and at one inch distant from the radiant source. It is also to be remarked that this second source of the X rays was nearer to the photographic plate only by 7-10ths inch minus 0·06 inch, the thickness of the tube, hence any effects due to them may be neglected, as indeed the results in the experiments on the inverse squares show.

The experiments described in this paper were made in the private laboratory of Professor Rood in Columbia University. Professor Rood not only gave me the use of his apparatus, which he had made the subject of a special investigation before investigating with it, but he also gave me the advantage of the experience obtained during his researches on the X rays.

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ON THE

# CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION.*

By DOUGLAS McINTOSH,
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IN a paper read before this Institute some months ago, Prof. MacGregor (*Trans. N. S. Instit. of Science*, ix., 101) showed how to obtain, by a graphical process, from observations of the electrical conductivity of a sufficient number of simple solutions of two electrolytes having a common ion, the data necessary for the calculation of the conductivity of a solution containing both electrolytes, according to the dissociation theory of electrolytic conduction ; and in order to test this theory, he calculated the conductivities of a series of mixtures of solutions of sodium chloride and potassium chloride, which had been measured by Bender. He found that for dilute solutions his calculations agreed with Bender's observations within the limits of experimental error ; but that, as the strength of the solution increased, the differences became larger, until, with a mixture of solutions containing each 4 gramme molecules per litre of salt (the strongest solutions with which Bender worked), a difference of 3·6 per cent was found. The method of calculation assumed that the ionic velocities of the constituent electrolytes were not changed by the mixing, and Prof. MacGregor attributed the differences between the calculated and observed values to the change which, as he pointed out, would probably be produced, in these velocities, by mixture.

At his suggestion I have made the observations described in this paper, with the object of determining (1) what the differences between the observed and calculated values are, in the case of mixtures of sodium and

potassium chloride solutions, of greater strength than those examined by Bender, and (2) how the calculated and observed values are related, in the case of solutions containing sodium chloride and hydrochloric acid,— electrolytes whose ionic velocities differ from one another much more than those of sodium and potassium chlorides.

The expression for the conductivity of a mixture of equal volumes of solutions of two electrolytes, 1 and 2, which contain $n_1$ and $n_2$ gramme-equivalents per unit of volume respectively, the ionisation coefficients of which, in the mixture, are $\alpha_1$ and $\alpha_2$, the molecular conductivities of which at infinite dilution are $\mu_{\infty 1}$ and $\mu_{\infty 2}$, and which so change in volume on mixing that the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions is $p$, is—

$$c = \frac{1}{2\,p}\left(\alpha_1\, n_1\, \mu_{\infty 1} + \alpha_2\, n_2\, \mu_{\infty 2}\right).$$

In order to calculate the conductivity of such a mixture, therefore, the seven quantities in this expression must be known. The ionisation coefficients, $\alpha_1$ and $\alpha_2$, are determined by the graphical process referred to above, from series of observations of the conductivities of simple solutions of the constituent electrolytes. The conductivities at infinite dilution are determined by similar observations with very dilute solutions. The concentrations may be determined by analysis, and the quantity $p$ by density measurements.

I intended at the outset to determine all these quantities myself, in order that the data of calculation might apply to exactly the same electrolytes. But owing to the fact that the electrolytic cell, to be used in the determination of conductivities at infinite dilution, although ordered months ago, did not arrive in time, I am compelled to use Kohlrausch's values of the conductivities at infinite dilution for the electrolytes examined.

### Determination of Conductivities.

Kohlrausch's well-known method with the telephone and alternating current was used. The apparatus was supplied by Queen and Co., of Philadelphia, and consisted of a German silver bridge-wire, about 3 metres long, wound on a marble drum. The wire was divided into 1000 parts, and had a resistance of about 1·14 ohms. I calibrated it by the method of Strouhal and Barus (*Wied. Ann.*, x., p. 326, 1880), and applied the corrections thus determined to the measured resistances. (The greatest correction that had to be applied during the experiments was one division).

Four coils, marked 1, 10, 100, 1000 true ohms, formed part of the apparatus, and were guaranteed correct to 0·1 per cent. The range of the resistances measured during the experiments, however, was so small that I needed to use only one of these coils (that of 100 ohms). Hence it was not necessary for me to test the relative accuracy of the coils. Nor did I need to test the absolute accuracy of the 100 ohm coil, as it was not necessary for me to express conductivities in absolute measure.

The cell used was a U-shaped one, with enlargements for the electrodes, of the kind shown in Ostwald's "Physico-chemical Measurements," p. 226, fig. 178. The cell and also the electrodes (each of which had an area of about 7 sq. c.m.), were smaller than ordered, and the latter were so thin as to be easily bent. No change of resistance, however, could be noticed for small bendings of the plates, which could be readily detected by the eye and avoided. The induction coil was quite small, and had a specially rapid vibrator. It was kept in an adjoining room, that the noise might not disturb the operator ; but after some practice it was found that measurements could be made without difficulty, even with considerable noise. Different kinds of batteries for working the coil were tried. The most satisfactory was found to be a small dry battery, made by the Mamisburg Electric Co., of the kind used for electric bells. With this apparatus the

"minimum" point on the bridge could be determined by the telephone to within ½ division. This, at the centre of the bridge, meant a possible error of 0·2 per cent, and at the point of the bridge farthest from the centre, used in my experiments, a possible error of 0·3 per cent.

### Temperature.

As the laboratory temperature varied considerably from day to day, the electrolytic cell was placed in a bath whose temperature was regulated by a thermostat of the kind described by Ostwald in his "Physico-chemical Measurements," p. 59. The resistances measured were so small that a sharp "minimum" was obtained when a water-bath was used. There was no necessity therefore for a petroleum-bath. The bath was stirred by a current of air from a small suction-pump, and the temperature kept as near to 18° C. as possible. When this temperature could not be exactly obtained, measurements of resistance were made at several near temperatures, and the temperature coefficients found. The coefficient was always about 2 per cent per degree.

The thermometer used was graduated to 0·1 degree centigrade, and could be easily read to 0·05 degree. This meant a possible error of 0·1 per cent in the determination of the resistance. The errors of the thermometer had recently been determined at the Physikalisch-Techniche Reichsanstalt, Berlin.

### The Platinising of the Electrodes.

The electrodes, after having been boiled in alkali and acid, were placed in a very dilute solution of chloroplatinic acid (HPtCl₆), and connected with a small battery, the direction of the current being frequently changed. When the electrodes had become covered with a black velvety coating, they were removed from the cell, and, in order to get rid of the chloroplatinic acid which adheres strongly to the platinum black, they were washed several times with boiling water. On one occasion, in the course of the experiments, the minimum point was found to be indistinct. The plates were accordingly re-platinised, and distinctness found to have been regained. The experiments previously made (those on potassium chloride) may have been affected by a slight error due to defective platinising.

### The Salts and Acids.

The potassium and sodium chlorides, obtained as chemically pure from Eimer and Amend, of New York, were further purified by re-crystallisation. Solutions of them were found to be neutral and free from sulphates and magnesia. Neither potassium nor other metals could be detected in the sodium chloride with the spectroscope. Sodium, but no other metal, could be detected in a flame coloured by the potassium chloride. The hydrochloric acid was obtained as chemically pure, and gave no residue on evaporation. It was free from sulphates.

### The Water used.

The water was doubly distilled, with addition of sodium hydrate, in a tin-lined retort, and condensed in a block-tin pipe, the first part of the distillate being rejected. It was stored in bottles which had been used for this purpose for several years. It gave no residue when evaporated, was neutral, and gave no colour with Nessler's reagent.

### Preparation and Analysis of the Simple Solutions.

The simple solutions were prepared by dissolving about the amount of salt required for the strongest solution, and subsequent diluting. The concentration in each case was determined by volumetric analysis. A solution of silver nitrate was used in estimating the chlorine in the potassium and sodium chlorides, and the amounts of salt present were calculated from the data thus obtained.

In making an analysis, 1 c.c. (or 5 c.c.) of the solution at 18° C. was drawn off by a pipette, placed in a flask, diluted, and coloured distinctly with neutral potassium chromate. Silver nitrate standardised at 18° C. was run in from a burette, and a glass bulb filled with potassium chromate of the same shade as the solution being analysed was held before the eye. The end point by this means could be seen quite sharply.

A solution of ammonia was employed for estimating the hydrochloric acid, with cochineal as an indicator.

The pipettes and burettes used were tested by weighing the water which they delivered. They were found to be accurate to 0·1 per cent.

To determine the accuracy of the volumetric analysis, a solution of sodium chloride was prepared, containing a known quantity of the pure fused salt. The results of the analyses were found to be correct to 0·1 per cent.

### Specific Gravity Determinations.

The object of specific gravity determinations was the finding of $p$ in the above expression for the conductivity. For this purpose it was necessary to find the specific gravity to the third decimal place only. Hence the determinations were made with a Mohr-Westphal balance which read to the fourth decimal place, and might be trusted in the third.

In all the mixtures examined $p$ was found to be practically equal to unity.

### Preparation of the Mixtures.

A 50 c.c. pipette, which had been carefully washed, and stood on filter-paper for some time, was rinsed out several times with one of the constituents of the intended mixture, whose composition and specific gravity had been determined. The pipette was filled to the mark, and the solution run into a clean and dry bottle. The pipette was then washed, and the other constituent placed in the bottle as before, care being taken to use the pipette in exactly the same manner in both cases. All mixtures were made at 18° C., and the same pipette was used for both solutions, in order that the mixture might consist of exactly equal volumes of them.

The conductivities of solutions were found to increase on standing, which was doubtless due to portions of the glass being dissolved. The conductivities were therefore measured as soon after the solutions were made up as possible.

### Capacity of the Electrolytic Cell.

To find the factor which would reduce the observed conductivities to the standard employed by Kohlrausch, viz., the conductivity of mercury at 0° C., the following simple solutions of potassium and sodium chloride were analysed, and their conductivities measured:—

| Potassium Chloride. | | Sodium Chloride. | |
|---|---|---|---|
| Concentration, (Grm.-molecules per litre. | Conduct-ivity, ×10⁸. | Concentration, Grm.-molecules per litre. | Conduct-ivity. ×10⁸. |
| 2·07 | 1854 | 2·06 | 1199 |
| 2·61 | 2281 | 2·56 | 1517 |
| 2·94 | 2521 | 2·83 | 1616 |
| 3·26 | 2767 | 3·37 | 1786 |
| 3·68 | 3040 | 3·70 | 1876 |
| 3·88 | 3187 | 4·29 | 1970 |
| | | 4·69 | 2025 |
| | | 5·12 | 2087 |

These values were plotted on co-ordinate paper with concentrations as ordinates and conductivities as abscissæ, and smooth curves were drawn between the points so as to obviate accidental errors. Conductivities were taken off these curves and compared with the numbers given by Kohlrausch (*Wied. Ann.*, vi., 146) for solutions of equal concentration, as shown in the accompanying table (see next column).

It will be noticed that the ratios in the above table are not the same for all solutions, but are practically the same for solutions of both salts of the same conductivity. The

### Potassium Chloride.

| Concentration Grm.-molecules. per litre. | Conductivity. Kohlrausch. | Observed. | Ratio. |
|---|---|---|---|
| 2 | 1728 | 1800 | 0·960 |
| 2·5 | 2122 | 2199 | 0·961 |
| 3 | 2480 | 2566 | 0·966 |
| 3·5 | 2822 | 2924 | 0·965 |

### Sodium Chloride.

| Concentration (Grm.-molecules per litre). | Conductivity. Kohlrausch. | Observed. | Ratio. |
|---|---|---|---|
| 2 | 1209 | 1277 | 0·946 |
| 2·5 | 1412 | 1500 | 0·941 |
| 3 | 1584 | 1675 | 0·946 |
| 3·5 | 1728 | 1815 | 0·952 |
| 4 | 1846 | 1928 | 0·957 |
| 4·5 | 1935 | 2000 | 0·968 |
| 5 | 1991 | 2066 | 0·964 |

variation of the ratio may have been due to some unknown defect of apparatus or mode of using it ; but as this source of error was equally operative in the case of solutions of both salts of the same conductivity, it would probably be equally operative also in mixtures of the same conductivity. Hence, in reducing the observed conductivity of a mixture of potassium and sodium chloride solutions to Kohlrausch's standard, the factor employed was the value of the ratio for the conductivity which the mixture was found to have, this ratio being determined from the above table by graphical interpolation. Bender found a similar variation in the ratio of his conductivities of solutions of these salts to Kohlrausch's conductivities for solutions of the same strength.

On comparing the observed conductivities of solutions of hydrochloric acid with conductivities of solutions of equal concentration, as given by Kohlrausch, the ratios were found to be practically uniform, and equal to 0·955. In the tables which follow all conductivities are expressed in terms of Kohlrausch's standard.

(To be continued).

## NOTICES OF BOOKS.

*Nitro-Explosives: a Practical Treatise concerning the Properties, Manufacture, and Analysis of Nitrated Substances, including the Fulminates, Smokeless Powders, and Celluloid.* By P. GERALD SANFORD, F.I.C., F.C.S., Member of the Society of Public Analysts; Consulting Chemist to the Cotton-powder Company (Ltd.); late Resident Chemist at the Gun-cotton Works, Stowmarket, and the Dynamite Works, Hoyle, Cornwall. London : Crosby Lockwood and Son. 1896. Pp. 274.

THIS work, which may with full justice be styled a "practical treatise," confines itself to the nitro-explosives —a very numerous class of the High Explosives. The substances which have been nitrated include cellulose in its various forms, glycerin, benzene, starch, jute sugar, phenol, wood, straw, treacle, and horse-dung !

The "danger area" at works for the manufacture of explosives is that portion devoted to the actual manufacture or mixing of explosive materials. The author judiciously recommends that all "danger-buildings" should be made of wood, and that they should be surrounded by mounds of earth or sand. Formerly danger-buildings were made bomb proof, which in case of an explosion greatly augmented the danger. This arrangement had been adopted at the works in the Hartz, where Chapman was torn to pieces. In powder-mills it was formerly customary to surround the danger-buildings with dense belts of trees. This precaution is utterly useless as against gun-cotton, dynamite, &c. With such agents the shock travels underground more rapidly than through the air. Thus at the great gun-cotton explosion at Stowmarket the windows of houses at some distance from the magazine were seen falling out of their frames before a sound was heard. The excellent caution is given that the clothing worn by the work-people upon the danger-area should have no pockets, which much reduces the chance of matches or steel articles being carried upon the danger-area. All tools used upon the danger-area should be of phosphor-bronze, and brass nails should be used not only in the erection of the building, but in the manufacture and closing of all packing-cases. As a matter of course the work-people change their shoes before entering a danger-building or the danger-area. The lightning-conductors, with which every danger-building and magazine should be fitted up, are of the construction proposed by Prof. Clerk-Maxwell.

Cordite, which has lately attracted considerable attention, is made at the Royal Gunpowder Factory at Waltham Abbey, and at one or two private factories ; it consists of gunpowder 37 per cent, nitro-glycerin 58 per cent, and vaseline 5 per cent. A solvent, such as acetone, is added to effect the solution of the gun-cotton.

The acid mixture used in the manufacture of gun-cotton at Waltham Abbey consists of 3 parts by weight of sulphuric acid, sp. gr. 1·84, and 1 part nitric acid, of sp. gr. 1·52.

We are reminded that celluloid is a variety of cellulose, and that much care is required in its manufacture. Some years ago a large packet of celluloid combs exploded in the guard's van on a German railway.

Melinite seems to be little else than picric acid, but its exact formula is not known. It seems highly probable that the expectations held out concerning melinite were greatly exaggerated. The French military authorities are not known to have employed it in actual warfare.

All persons connected with the production and use of high explosives will find Mr. Sanford's work invaluable.

*Les Actualities Chimiques.* Review of the Progress of Pure and Applied Chemistry. (Appearing six times yearly). Published under the direction of Charles Friedel, of the Institute. Paris : George Carré.

OUR readers are, of course, aware that among our French neighbours the actual is not, as with us, the demonstrably existing, in contradistinction to the imaginary or the conjectural, but that which is at the present moment occurring or attracting attention as different from the past or the future.

Of the lectures or essays before us particular attention is due to the two first, that is, one by Prof. Schützenberger on the critiques of Dr. Hinrichs on the "Atomic Weights as determined by Stas" and that of Dr. Wyrouboff on the "Periodic Classification of the Elements."

Dr. Hinrichs is pronounced here a mathematician rather than an experimentalist. His fundamental idea is that of the unity of matter. For him, and in some degree for all of us, the elements are the result of the condensation, according to certain laws, of a single principle which he names pentogen, and which we may identify with the *protyle* of the glorious friar Roger Bacon, and of Mr. W. Crookes in our own time.

This, Prof. Schützenberger says, is the theory of Prout in support of which Dumas brought forward his determinations. After the publication of the Memoir of Dumas the hypothesis of Prout seemed established. Yet Stas threw back everything into uncertainty. He put forward "determinations made with exceptional care, a minute criticism of the causes of error of which they admit, a precision which has never been reached before or since, and established with a certainty against which

it seemed difficult to contend that the atomic weights, far from being multiples of the same magnitude, as 0·5 or 0·25, have among themselves no single or rational relation."

Hinrich appeals from this judgment. He does not indeed criticise the material accuracy of the experiments of the Belgian chemist—a task, we may add, for which his aptitude is, to say the least, not proven—but he seeks to show that these beautiful experiments do not admit of the consequences which have been drawn from them.

The characteristics of the experiments of Stas are :—

1. The minute care introduced in the purification of the substances employed.

2. In operating upon large but variable quantities of matter. Thus, for lead he performed ten experiments, with quantities of lead varying from 103 to 250 grms.

For silver he effected 9 determinations, using doses of silver of from 77 to 404 grms.

Dr. Hinrichs argues that the mean of a series of experiments, the results of which differ from each other by small quantities, have not the chance of approaching nearer to the truth than any one of them. It is evident that if all the determinations are above, and unequally above, the truth, the mean will be less exact than the smallest number found.

In addition to the mathematical strictures of Dr. Hinrichs, he brings forward another kind, more intelligible to chemists.

Whenever we decompose, by heat, a compound which is thus resolved into a fixed and a gaseous or volatile constituent, it is extremely difficult to eliminate the last traces of the volatile product, a fraction of which remains energetically fixed on the non-volatile residue, and, although minimal, may be rendered sensible by delicate reactions. In support of this assertion we might cite very distinct observations controlled by a great number of experiments.

It is generally admitted that pure copper nitrate, if heated progressively to nascent redness, becomes pure cupric oxide as a fixed residue when every trace of nitrous vapour has disappeared. But if, after having heated such an oxide to dull redness for a long time in a current of air, we reduce it with hydrogen, it is always found that the weight of water formed is less than that which corresponds to the loss undergone by the oxide reduced to the state of copper, and that we calculate according to this loss on admitting that water is formed of 8 parts of oxygen and 1 part of hydrogen. This excess of loss undergone by the cupric oxide of the nitrate is due to nitrogen, which remains energetically fixed upon the product.

Hence it results necessarily that all the syntheses of water effected with the oxide of the nitrate give too high a value for the equivalent of oxygen with reference to $H = 1$, or too low a value with reference to $O = 16$.

With oxide of copper obtained by the direct combination of copper this discrepancy no longer exists.

Nothing proves that on the decomposition of potassium chlorate by heat the expulsion of the oxygen is absolute, so that what is calculated as potassium chloride does not retain obstinately a certain dose of oxygen. According to the great generality of facts of this kind, the inverse seems to us scarcely possible. Potassium chlorate, heated for a long time to nascent redness, until the cessation of all escape of gases, and even longer, gives with water a reaction of potassium chloride which, in presence of hydrochloric acid, decomposes extract of indigo in heat, and if it is thus the very foundation of the experiments of Stas is shaken, precise as they appear, and the entire edifice must be reconstructed.

When Stas transforms a known weight of pure silver into dry, and even fused, nitrate, and, from the weight of the nitrate found, deduces the atomic weight of nitrogen, we cannot exclude the suspicion that the residual nitrate may retain a fraction of the nitric acid used in excess to dissolve the silver, and that this residue in place of being $NO_3Ag$ really represents $NO_3Ag$ and $\delta NO_3H$.

If the cause of error which we thus point out is of a magnitude capable of seriously affecting the numbers found, there will be room to proceed to a revision. Perhaps we may then return to the theory of Prout and of Dumas.

We shall next proceed to consider the periodic classification of the elements.

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*Chemical Notes and Equations.* By G. H. GEMMEL, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. Edinburgh: Livingstone, Thin. Dublin: Fannin and Co. Glasgow: Stenhouse. Pp. 244.

THIS is by no means an unfavourable specimen of the class to which it belongs,—elementary chemical treatises, in which it would be very difficult to point out any error, either in fact or in inference, but which all the while leave us in some doubt concerning their *raison d'être*.

The author addresses himself especially to medical students, and hopes that what he has written may diminish the necessity for taking notes at lectures.

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*Rheumatism, its Nature, its Pathology, and its Successful Treatment.* By T. J. MACLAGAN, M.D., Physician in Ordinary to their Royal Highnesses Prince and Princess Christian of Schleswig-Holstein. Second Edition. London: Adam and Charles Black. 8vo. 1896.

THE work before us is distinctly and purely medical. The author traces a parallelism between malaria and rheumatism, and shows that in the latter salicin plays as successful a part as does quinine in the former. He points out that the willow, from which salicin is obtained, flourishes particularly in the cold damp districts which are the home of rheumatism.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

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NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 1.

Determination of Sulphurous and Sulphuric Acids in the Products of the Combustion of Coal-gas.—M. Dennstedt and C. Ahrens.

Use of Solutions of Iodine for the Volumetric Determination of Solutions of the Alkaloids.—Dr. C. Kippenberg.—By occasion of the publication of an inquiry entitled "Contributions to the Isolation, Determination, and Chemical Diagnosis of Alkaloids and Glykosidic Substances in Judicial Cases, with especial reference to their Recognition in Putrescent Human Remains," I have made some investigations on the use of a solution of iodine obtained by dissolving free iodine in water by means of a solution of potassium iodide. It was used for the separate determination of alkaloids, and it appeared that only the free iodine of the standard liquid comes into action for the production of the insoluble periodide composed of the alkaloid. This compound is produced by the hydriodate of the alkaloid and of iodine, whilst the potassium iodide of the standard liquid remains in the first place unchanged, and is only subsequently affected by the decomposition of the water induced by the formation of the alkaloid hydriodate. The author gives an account of experiments with narcotine, strychnine, and atropine in different solutions and degrees of concentration.

**Optical Determination of Alcohol and Extract in Wines.**—Prof. Dr. E. Riegler.—The author makes use of Pulfrich's refractometer, which permits of a determination of the indices of refraction as far as five decimal places. The three indices required are that of the wine, of the solution of the extract, and of distilled water. The author gives a table useful in the application of his method. The constants for beer are, the same as those for wine.

**Method for the Determination of Uric Acid.**—Prof. Dr. E. Riegler.—This method depends on the reduction of Fehling's solution to red cuprous oxide in heat. The author first determines the reductive value of uric acid with Fehling's liquid. One grm. of uric acid may be regarded as a mean to represent 0·8 grm. copper. This experimental result agrees very closely with the calculated quantity 0·7556 copper. He separates the uric acid from urine according to Fokker's process as ammonium urate. The reduced cuprous oxide may be weighed as such and calculated as copper, or it may be reduced to metallic copper and weighed as such. The quantity of uric acid required is found by multiplying the weight of copper found by 1000/0·8 = 1·25.

**Determination of the Purity of Oil of Bergamot.**—Prof. Dr. A. Bornträger.—This paper is of little general interest.

**Blackening of Vegetables Preserved in Sheet Tin Boxes.**—Dr. A. Rossing.—This blackening seems to have been first observed by Beckurts (*Chemiker Zeitung*, 1889) and Beckurts and Nehring (*Apotheker Zeitung*, 1890). The dark coating observed especially on the inside of the boxes is traced to the formation of tin sulphide. It occurs only in spots where the vegetables come in direct contact with the tin. It is not confined to cans where the contents are spoiled, but also in such as contain vegetables agreeable to taste and smell. It has never been observed in cans containing beans. The tin itself sometimes becomes dissolved. Weber (*Chemiker Zeitung*, 1892) detected in pumpkins 0·054, 0·444, in cherries 0·414, in peaches 0·324, in tomatoes 0·140 stannic acid per kilo., but in peas only 0·069 and 0·043. Vegetables and fruits containing tin have been examined by Van Hamel Roos and Wefers Bettink (*Chemiker Zeitung*), who observed that 270 soldiers at Utrecht became ill after consuming canned vegetables in which 0·019 to 0·072 grm. tin per kilo. was detected. The author regards the proposal of preserving vegetables and fruits in glass bottles as impracticable on a commercial scale. He approves of the suggestion of coating the cans internally with varnish. This procedure has been officially adopted by the Dutch Admiralty.

**Refractive Power and Density of Dilute Solutions.**—W. Hallwachs (*Ann. der Phys. und Chemie*).—There is here merely a reference to the original.

**Influence of Solvents upon the Rotative Power of Organic Substances.**—P. Freundler (*Ann. de Chim. et Phys.*).—The author has especially investigated the tartaric ethers. The abstractor points out that, in many cases in which strong deviations of the specific rotatory power were observed as a consequence of the action of certain solvents, the determination of the molecular weight cryoscopically or by determination of the vapour tension gave very abnormal values. The author infers that in such cases there ensues a dissociation of the rotating substance.

**Use of the Critical points of Liquids as a Criterion of their Purity.**—R. Pictet (*Comptes Rendus*, cxx., 43).

**A Decision on the Solubility of certain Sparingly Soluble Bodies from the Electric Conductivity of their Solutions.**—F. Kohlrausch and F. Rose (*Sitzungsb. der Phys. Math. Kl. der Konigl. Acad. zu Berlin*).—According to these communications the experimentalist can at any time in a few seconds determine, by means of an electric current, the condition of a solution and follow the course of its formation. The contamination of the solutions and the weighing of small quantities in large capsules are ex-cluded. The solution does not need to be separated from undissolved matter, and it may be even turbid without affecting its conductivity.

**New Mercurial Air-pumps.**—New constructions have been introduced by E. Lueke, of Berlin, as here figured; by G. W. A. Kahlbaum (*Annalen der Phys. und Chem.*); Schulze-Berge (*Ann. der Phys. und Chem.*), and German patent 72,329, a safety-valve for water-pump, H. Berlemont (*Bull. de la Soc. Chim. de Paris*).

**On Balances and Weights.**—W. H. F. Kuhlmann (*Chemiker Zeitung*) has devised a rapid balance with telescope readings. At its mean load the balance comes to an equilibrium in nine seconds. Herzberg, of the firm Paul Bunge (*Chem. Zeit.*), objects to Kuhlmann's construction. A preliminary balance, to avoid the re-adjustment of the larger weights, is proposed by Schiermann (*Chem. Zeit.*). A new system of weights has been proposed by the same author (*Chem. Zeit.*). It proceeds from 1 c.g., and has in the same series the double and quadruple weight marked 2 and 4. The octuple weight is the unit of the following series.

**Adjustment and Suspensions for the Terminal Knife-Edges of Balances of Precision.**—L. Armbruster.—(German patent, 72,524).

**Apparatus for Fractionated Distillation.** — Several new arrangements have been proposed by Marius Otto (*Bull. Soc. Chim. de Paris*); Varenne (*ibid.*); H. Wislicenus (*Berichte*); H. Schulz (*Berichte*); F. Anderlini (*Bull. Soc. Chim. de Paris*).

**New Laboratory Appliances.** — H. Lœmer (*Journ. Prakt. Chemie*) describes a new stirring apparatus on the same principle as Witt's centrifugal agitator, applicable even in small flasks with narrow necks. The same author describes a water-bath with a movable ring having the construction of an iris screen.

**New Apparatus.** — J. Volhard (*Liebig's Annalen*).—The appliances described require the accompanying cuts.

**An Arrangement for the Automatic Exhibition of a Gas Flame after a given time.**—P. N. Raikow.—(From the *Chemiker Zeitung*).

**Glass Cocks with a Safety Arrangement**—E. Greiner.—(A trade catalogue). The plug is held in its place by an elastic tissue.

**An Extraction Apparatus.** — L. Etaix.—From the *Bulletin de la Soc. Chim. de Paris.*

**A Bottle with Liquid Joint.**—F. Meyer (*Zeit. fur Angewandte Chemie*).—The bottle is adapted for washing, drying, and absorbing gases.

**A New Sulphuretted Hydrogen Apparatus.** —W. Gallenkamp (*Chemiker Zeitung*).

**Glass Vessels for preserving Substances sensitive to Light.** — Hr. Biltz (*Pharm. Central Halle*).. — The author concludes, from his experiments, that coloured glass (black or brown) does not entirely exclude the chemically active rays of light.

**Luteol, a New Indicator.**—W. Autenrieth (*Archiv der Pharmacie*)—Already inserted.

**On Ether.** — Lassar Cohn (*Liebig's Annalen*. — The author's experiments have the view of obtaining an ether absolutely free from aldehyd.

**Determination of Chlorine in Bromine.**—Hr. Erchentrecher (*Zeit. fur Ankewandte Chemie*).—The author weighs off 20·6 grms. or sodium bromide free from chloride, and dissolves so as to make up 1 litre; 25 c.c. of this solution are added in an Erlenmeyer flask to 6 grms. of the bromide in question, and evaporated. The solution is boiled up, rinsed into a capsule, evaporated to dryness, ignited gently, and weighed. The proportion of chlorine can be found by means of a table.

On Technically Pure Starch Sugar, and on Wine obtained with its Use. — Prof. Dr. R. Fresenius. — A study referring to the German laws on the use of improper materials in the manufacture of foods and beverages. The author contends that starch sugars and their products, though not technically pure, are not objectionable on hygienic grounds.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1912.

## NOTES ON THE REPLACEMENT OF CHLORINE IN THE CHLORIDES OF THE NON-METALS AND METALLOIDS BY BROMINE AND IODINE.

### By H. LLOYD SNAPE, D.Sc, Ph.D.

R. BRIX (*Liebig's Annalen*, 1884, ccxxv., 146), B. Kœhnlein (*Ibid.*, ccxxv., 171), and H. Spindler (*Ibid.*, 1885, ccxxxi., 257) have shown that the elements chlorine, bromine, and iodine replace one another in many *organic* haloid compounds, when these are heated with metallic chlorides, bromides, and iodides. The object of the experiments detailed below was to determine whether the chlorides of the *non-metals* would not undergo a similar decomposition when heated with potassium bromide and potassium iodide respectively.

G. Gustavson (*Berichte*, 1874, vii., 128; *J. d. Russ. Chem. Gesellsch.*, 1881 [1], 288) found that carbon tetrachloride was converted, by aluminium iodide in carbon disulphide solution, into carbon tetriodide, and, in the paper to which reference has been made above, Spindler showed that carbon tetrachloride may be converted into the corresponding iodide by treatment with potassium iodide.

G. Rauter (*Liebig's Annalen*, 1892, cclxx., 246) investigated the behaviour of silicon tetrachloride towards a large number of mineral compounds of varied types, and found, *inter alia*, that this chloride was but little attacked by potassium bromide and potassium iodide. The chemical changes which did take place to a slight extent, he considered to be indicated by the equations—

$$2SiCl_4 + 8KBr = 8KCl + Si_2 + 4Br_2.$$
$$2SiCl_4 + 8KI = 8KCl + Si_2 + 4I_2.$$
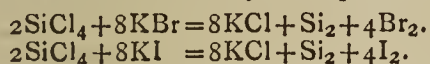
E. Bamberger and J. Philipp (*Berichte*, 1881, xiv., 2643) described the formation of arsenious iodide by the addition of a strong aqueous solution of potassium iodide to a hydrochloric acid solution of arsenious oxide.

I anticipated that the strongly basic element potassium would readily remove chlorine from its comparatively unstable combinations with the non-metals, and that the latter when liberated would probably unite with the bromine or iodine simultaneously set free.

Owing to the readiness with which most of the non-metallic haloids are attacked by water, it was obviously necessary, in the majority of cases, to work with absolutely dry materials and out of contact with air; hence my experiments were carried out in sealed tubes. Moreover, as the non-metallic bromides and iodides which I hoped to obtain are even when dry in many cases decomposed by heat, but at temperatures not always stated in the literature, it would evidently be advantageous to have the contents of the tubes under observation, so that in the event of such decomposition the liberation of bromine or iodine would at once be recognised, and the temperature might be reduced; hence some of the sealed tubes were heated in a deep glass bath containing paraffin. As, should the undecomposed chloride remain behind with the bromide or iodide of the non-metal formed, the separation would be difficult, I employed in all instances an excess of the metallic salt.

Proceeding in this way I found that, by means of *potassium bromide*, sulphur monochloride and arsenic trichloride were partially converted into their respective bromides, but, on the other hand, no similar conversion could be effected by the action of the first-named compound upon carbon tetrachloride and phosphorus trichloride. Carbon tetrachloride behaved in an analogous manner to silicon tetrachloride as described by Rauter; phosphorus trichloride was apparently unchanged.

I also further examined the behaviour of the same potassium salt towards the trichloride of the metalloidal element antimony.

R. W. Atkinson (*Journ. Chem. Soc., Trans.*, 1883, xliii., 289) had already shown that on mixing strong solutions of antimony trichloride and potassium bromide, or of antimony tribromide and potassium chloride, the same compound ($K_3SbBr_3Cl_3$) was obtained. This was, however, decomposed by heat-yielding vapours in equivalent proportions of antimony trichloride and tribromide. Hence I expected that on passing the vapour of antimony trichloride over a long layer of potassium bromide, heated to a sufficiently high temperature to decompose the double salt, most, if not all, of the antimony trichloride would be converted into antimony tribromide. This change actually occurred.

The results of the similar experiments conducted with *potassium iodide* are as follows :—Phosphorus trichloride, arsenic trichloride (Bamberger and Philipp had used hydrochloric acid solution of arsenious oxide), and antimony chloride, were readily converted into their respective iodides; carbon tetrachloride was only in part attacked, and yielded only free carbon and iodine, again behaving analogously to silicon tetrachloride; sulphur monochloride was much more completely decomposed, and also yielded no definite iodide, but only the elements sulphur and iodine.

For the convenience of comparison I repeated the method of Guthrie (*Journ. Chem, Soc., Trans.*, 1862, xiv., 57) for the preparation of sulphur moniodide, and I have made a few notes on this which will be found below.

#### Sulphur Monochloride and Potassium Bromide.

5·4 grms. of sulphur monochloride of b.-p. 136°—8° were heated with 12·7 grms. of dry potassium bromide (only 9·5 grms. of the latter theoretically required for mutual decomposition), first for one hour at 100° C. At this temperature there was no apparent change. The temperature was then maintained for two hours at 180° to 190°, and then for over seven hours at 200° to 220°. The tube stood for some days before being opened. The contents, which were of a pasty consistence, were extracted with carbon disulphide, and the liquid extract was subjected to fractional distillation. Bromine began to come over at 60°, and the temperature rose steadily up to 230°, when a black mass of sulphur remained behind. Between 160° and 220° there passed over 5·4 grms. of a dark red liquid, which decomposed, on re-distillation, some bromine first passing over and some sulphur remaining behind. This corresponds to the unstable compound $S_2Br_2$, which Pattison Muir (*Journ. Chem. Soc., Trans.*, 1875, xxviii., 845) held was formed by the direct union of sulphur and bromine. Had this been formed in the present case, reaction must have taken place in accordance with the equation—

$$S_2Cl_2 + 2KBr = 2KCl + S_2Br_2.$$

Theoretically, 9 grms. of sulphur monobromide should thus have been produced, had the reaction been quantitative; but doubtless some portion of this compound, if formed at all, underwent dissociation during the first distillation.

#### Sulphur Monochloride and Potassium Iodide.

3·8 grms. of sulphur monochloride were treated with 12 grms. of perfectly dried potassium iodide (one-third more than the theoretical quantity of the latter). Some reaction took place as soon as the substances were mixed, a violet-red colour being acquired. In order to render the reaction more complete, the whole was heated for rather more than two hours at 60° to 80°. The cooled residue was reddish brown in colour, compact, and very hard, and

contained a large number of small lustrous crystals. The whole mass was repeatedly extracted with carbon disulphide, deep violet solutions being obtained. The entire extract was then distilled to remove excess of solvent, and the concentrated solution cooled. The first crystals, which were dark in colour and not unlike iodine, were re-dissolved in carbon disulphide, and by fractional re-crystallisation portions A, B, and C were successively obtained. From the original mother-liquor two additional lots of crystals, D and E, were separated. The crystals E, which separated last from the original solution, consisted of almost pure sulphur, and were yellow in colour and transparent. The other crystals were all very dark in colour, and though C and D consisted of well-formed octahedra, and appeared at first sight to be homogeneous, they proved to be constituted of mere mixtures of sulphur and iodine. On merely standing in air at ordinary temperature, they lost iodine, and free sulphur remained behind. This afforded a ready means of determining the percentages of sulphur they respectively contained, though for analytical purposes the decomposition was facilitated by heating on the top of a steam-oven. Portions A, B, C, and D were thus found to contain only 0·46, 0·24, 1·2, and 1·14 per cent of sulphur respectively. A determination of sulphur in another portion of the crystals D was made by Carius's method, and gave 1·4 per cent.

The above results are most easily explicable on the hypothesis that the main reaction is—

$$S_2Cl_2 + 2KI = 2KCl + S_2 + I_2.$$
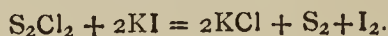
From a solution of sulphur and iodine in carbon disulphide, iodine being the less soluble, the first crystals to separate out would naturally consist mainly of this element, the later products of crystallisation containing more sulphur, and finally pure sulphur would be obtained. This would accord with the actual experimental results.

The above result led me to investigate the reaction by which F. Guthrie (*Journ. Chem. Soc., Trans.*, 1862, xiv., 57) first prepared (?) sulphur moniodide. His method consisted simply in mixing sulphur monochloride and ethyl iodide in equivalent proportions, and removing the ethyl chloride formed by applying gentle heat. The only evidence offered in support of the view that sulphur moniodide had been produced was an analysis of the residue; but the ethyl group having combined with chlorine, this residue would necessarily contain sulphur and iodine in equi-atomic proportions, *whether combined or uncombined :* $2C_2H_5I + S_2Cl_2 = 2C_2H_5Cl + S_2 + I_2.$

### *Sulphur Monochloride and Ethyl Iodide.*

2·3 grms. of sulphur monochloride and 6·1 grms. of ethyl iodide were introduced into a sealed tube, which was then exposed to the sun's rays for several days, but was not subjected to any artificial heat. The liquid gradually deepened in colour, and on the second day crystals separated. After an interval in all of five days, the drawn-out end of the tube was broken and attached to a calcium chloride tube, and the ethyl chloride was allowed to spontaneously evaporate. Any residual ethyl chloride was removed by connecting the tube to a filter-pump, and warming the contents by the hand. The dry crystalline mass which remained smelt strongly of onions (probably due to a trace of some compound of a mercaptan nature). Though the crystals appeared at first sight to be homogeneous and dark, an examination under a microscope showed that they consisted of a mixture of light yellow transparent crystals of sulphur and black opaque crystals of iodine, and, on treating a small quantity on a watch-glass with ether, only the former remained unchanged in the original rhombic crystals. 0·3894 grm., after the iodine had been removed by standing on the top of a water-oven, and later in a desiccator, yielded a residue of 0·0785 grm., equivalent to 20·16 per cent of sulphur. The percentage of sulphur required for the formula $S_2I_2$ is 20·13. Guthrie obtained, by fusing his crystals with

potassium nitrate and sodium carbonate, 20·28 per cent. Such analyses, however, do not afford any proof of the existence of the compound $S_2I_2$. As stated above, whether chemical union has occurred or not, equivalent proportions of sulphur and iodine necessarily constitute the residue after the expulsion of ethyl chloride.

### *Carbon Tetrachloride and Potassium Bromide.*

4 grms. of carbon tetrachloride of b.-p. 76·5° were heated with the equivalent quantity of potassium bromide in a sealed tube, for seven hours at 200°. After cooling, the bulk of the solid was seen to have acquired a pale yellow colour ; small dark-coloured particles were also visible in the mass. The whole was extracted with ether, which took out bromine, and on evaporation left only a mere trace of a dark red substance. Hence carbon tetrabromide was not formed. The residue was grey, and contained, in addition to the white potassium salts, a small quantity of dark brown carbonaceous substance insoluble in water.

### *Carbon Tetrachloride and Potassium Iodide.*

2·7 grms. of carbon tetrachloride were similarly treated with an equivalent quantity of potassium iodide, for three and a half hours at 200°. During this treatment free iodine was evidently evolved, and the reddish brown mass obtained on cooling contained crystals of iodine. The whole was extracted in a Soxhlet's apparatus by means of ether, and the ethereal extract was evaporated. Only a very small quantity of a dark-coloured substance was obtained, and this gave off iodine on being heated, and left a black residue, probably consisting of carbon.

The residue, which was left after complete exhaustion with ether, was still light brown in colour, and, on addition of water to dissolve the potassium salts, there was a small insoluble residue, evidently consisting of a carbon compound or amorphous carbon.

### *Phosphorus Trichloride and Potassium Bromide.*

4·6 grms. of phosphorus trichloride of b.-p. 76° to 78° were heated with a slight excess of potassium bromide, for eight hours at 200° to 220°. After the sealed tube had stood for a few days at the ordinary temperature, it was opened, and the contents, consisting of a moist greyish mass, were exhausted by chloroform. The chloroform extract was then distilled, when the greater part passed over at 61° ; then the temperature rose to 63°—64°, and finally a very small fraction passed over at 65°. Thus the temperature at no time reached even the boiling-point of phosphorus trichloride, much less that of the tribromide (175°). The distillates fumed strongly in contact with air, and evidently contained unaltered trichloride which had passed over with the chloroform.

### *Phosphorus Trichloride and Potassium Iodide.*

As soon as phosphorus trichloride was mixed with potassium iodide there was a slight evolution of heat, and the mass acquired an orange colour. To render the reaction more complete, the whole was heated for two and a half hours at about 200°. The phosphorus triiodide, which was at once recognisable after cooling the tube, was extracted by carbon disulphide, and separated from this solution, after evaporation *in vacuo*, in crystals which possessed the characteristic red colour and melted at 55°. This reaction was in accordance with the equation $PCl_3 + 3KI = 3KCl + PI_3.$

### *Arsenic Trichloride and Potassium Bromide.*

Five grms. of arsenic trichloride (b.-p. 131·5—132·5°) were heated with excess of potassium bromide for more than ten hours at from 180° to 220°. The cooled tube-contents, which had a slight brown colour, were exhausted with chloroform, and the extract was then fractionally distilled. The last fraction passed over between 130° and 90°, and weighed 3·8 grms. This was surrounded by a

freezing mixture, when the whole became apparently one solid mass. As the temperature was allowed to rise, a part became fluid again, so that at 0° only about two-thirds of the original mass of crystals remained, at 2° only about one-third, and at 11° the whole had become fluid. The melting-point, like the boiling-point of the bromide, had evidently been reduced by the presence of unaltered chloride. As the quantity was too small for further fractionation, the crystals which remained, as described above, at 2° were analysed by dissolving in excess of sodium-hydrogen carbonate solution and titrating with standardised iodine solution in presence of starch. The crystals were found to contain 25·92 per cent As, which indicated that the arsenic bromide still contained 12 per cent of arsenic chloride; the calculated percentage of arsenic in the bromide and chloride being 23·81 and 41·32 respectively. The following reaction had thus occurred, though not quantitatively :—

$$AsCl_3 + 3KBr = 3KCl + AsBr_3.$$
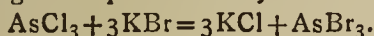
### Arsenic Trichloride and Potassium Iodide.

Bamberger and Philipp having already shown that arsenic iodide is formed on the addition of an aqueous solution of potassium iodide to a solution of arsenious anhydride in hydrochloric acid, it was practically certain that arsenic chloride and potassium iodide would readily attack one another in the dry state, but to make this series of reactions complete, the actual experiment was tried. On mixing these two compounds at the ordinary temperature partial reaction occurred, and heat was evolved. After heating the mixture in a sealed tube to about 240° and then cooling, the characteristic highly lustrous red tables were seen to have been formed throughout the mass. They were readily re-crystallised from ether or benzene; separating from benzene in especially fine crystals.

### Antimony Trichloride and Potassium Bromide.

After heating these two substances, both being in dry condition, with one another, no antimony tribromide could be extracted by solvents. Hence in all probability the same compound $(SbK_3Cl_3Br_3)$ had been formed, as Atkinson obtained on bringing the same two reagents together in presence of water. As Atkinson states this compound decomposes on heating, with evolution of equivalent quantities of antimony trichloride and antimony tribromide, the conversion of the former into the latter might be effected by passing it over a long layer of heated potassium bromide.

A fractional distillation flask, containing 10 grms. of crystallised antimony trichloride, was connected with a long hard glass tube lying in a combustion furnace, and along which 20 grms. of potassium bromide were evenly spread in a thin layer. The further end of the combustion-tube was constricted and bent downwards into another fractional distillation flask. The potassium bromide having first been heated, and the pressure greatly reduced throughout the apparatus by means of a water air pump, the antimony trichloride was driven over slowly. The distillate condensed in the further flask to a crystalline mass. This was re-distilled to free from any potassium or oxy-salts; 8·3 grms. passing over between 220° and 250°; this last was again fractionated, when about one-half passed over between 230° and 240°, and the remainder between 240° and 250°. The last few drops were separately collected, and were found by titration with standardised iodine solution, after dissolving with the aid of tartaric acid and addition of excess of sodium-hydrogen carbonate, to contain 38·41 per cent antimony. This would indicate (as SbBr₃ and SbCl₃ contain respectively 33·7 and 53·39 per cent Sb) that this portion contained 76·1 *per cent of antimony tribromide.* The fraction boiling between 230° and 240° yielding, on the other hand, 45·19 per cent Sb, equivalent to only 41·6 per cent of antimony tribromide in this mixture.

### Antimony Trichloride and Potassium Iodide.

These two compounds were heated together for two to three hours at about 200°, when complete mutual decomposition readily occurred. $SbCl_3 + 3KI = 3KCl + SbI_3.$ The antimony iodide was readily extracted by carbon disulphide, and was obtained from this solution in characteristic highly lustrous red crystals, which melted at 165°.

University College of Wales, Aberystwyth.

# STUDY ON CAST VANADIUM AND VANADIUM CARBIDE.

## By HENRI MOISSAN.

WE have formerly indicated that vanadic acid can be reduced by means of coke in the electric furnace, yielding cast vanadium, which contains from 17 to 25 per cent of carbon. Thanks to the kindness of M. Heeren, who has placed at our disposal a considerable quantity of ash derived from a vanadiferous coal, we have been able to continue and extend these researches.

*Treatment of the Vanadiferous Ash.*—The ashes mixed with fragments of coal, as sent me, contained about 8 to 10 per cent of vanadic acid. They were roasted in the muffle so as to destroy all the carbonaceous portions, when their proportion of vanadic acid was increased to 38 per cent.

Five hundred grms. of ash were placed in a 2-litre flask on the sand-bath, and attacked with nitric acid, to which was added, at considerable intervals, a small quantity of hydrochloric acid. The soluble matter was taken up in water, and the insoluble residue was wasted. After filtration through cloth, all the liquids were mixed together and evaporated to dryness. The residue was dissolved in ammonia diluted to one-tenth, yielding a first solution of ammonium vanadiate, which was then precipitated with nitric acid, to furnish crude vanadic acid.

The insoluble residue was exhausted with ammonia diluted to one tenth, yielding a further quantity of vanadiate which was treated in the same manner with nitric acid.

The crude acid thus obtained was purified by L'Hôte's method (*Ann. de Chim. et de Phys.*, Series 6, xxii., 407, 1891). The vanadium is transformed into vanadyl chloride, which latter is decomposed with water.

The vanadyl chloride was obtained at 250°, and the rectification was effected by fractions of 1500 grms. by means of a bulb-apparatus. Vanadyl chloride distils at + 126·5°, the figure indicated by L'Hôte.

By decomposition with water we obtain pure vanadic acid, which is then dried with care.

*Preparation of Cast Vanadium.*—Vanadic acid was mixed with the charcoal of sugar, finely pulverised, in the following proportions :—

| Vanadic anhydride | .. .. | 182 grms. |
| Sugar charcoal | .. .. .. | 60 ,, |

Of this mixture 300 grms. were heated in the electric furnace with a current of 900 ampères and 50 volts. The duration of the experiment is five minutes. In this manner we obtained a highly carburetted vanadium, which on analysis gave the following figures :—

|  | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Carbon .. | 10·5 | 13·8 | 11·6 | 16·2 | 15·9 |

In another series of experiments we employed :—Vanadic anhydride, 100; charcoal, 20; and we obtained castings containing, per cent, 9·9, 9·2, 9·83.

All these experiments have been made in tubes of coke. It is necessary to employ an intense current of very short duration, because the anhydride easily fuses and completely moistens the coke of the tube. In this case the carburation is very rapid.

When we attempted to refine cast vanadium by means of vanadic anhydride all our experiments have proved fruitless, by reason of this easy liquefaction of vanadic acid. The beautiful researches of Prof. Roscoe have, moreover, shown that the preparation of vanadium is one of the most difficult problems of mineral chemistry.

The powerful affinity of vanadium for nitrogen further augments these difficulties. It is useful to reach a very high temperature to effect the destruction of the nitride.

On heating pure vanadic acid for two minutes only in a coke tube, with a current of 1000 ampères and 60 volts, and taking care to keep up a constant current of hydrogen in the coke tube, we succeeded in obtaining cast vanadium not containing more than 5·3 to 4·4 of carbon.

Another specimen, heated for three minutes, gave us 7·42 of carbon.

*Properties of Cast Vanadium.*—Cast vanadium containing 5 per cent of carbon has a white colour, a brilliant fracture, metallic, not oxidisable in the air, and a sp. gr. of 5·8 at +20°.

Prof. Roscoe found 5·5 for vanadium containing traces of oxygen, and 1·3 per cent of hydrogen.

This cast metal burns with incandescence in oxygen at a red heat. Chlorine attacks it at a dark red heat without incandescence. With nitrogen it combines readily. In a general manner this cast metal is attacked by acids more readily than the definite carbide of which we have to speak. Hydrochloric acid attacks it neither in cold nor in heat. whilst sulphuric acid, concentrated and boiling, attacks it very slowly. Its other properties are comparable with those of Prof. Roscoe's vanadium.

*Preparation of Vanadium Carbide.*—If we heat, in the electric furnace, vanadium anhydride mixed with sugar and charcoal in a tube of coke for nine to ten minutes (900 ampères and 50 volts), we obtain a regulus formed of a definite vanadium carbide, which gives up a small quantity of graphite at the moment of its solidification.

*Properties of Vanadium Carbide.*—CVa is volatile when strongly heated in the electric furnace. Its melting-point is a little higher than that of molybdenum. In the liquid state it has a metallic aspect. Its sp. gr. is 5·36. It scratches quartz easily, and occurs in beautiful well-defined crystals.

Chlorine attacks it with incandescence above 500°, yielding a liquid chloride easily volatile. In oxygen it burns at a dark red heat with a lively incandescence. It does not combine with sulphur at the melting-heat of glass. Nitrogen and ammonia attack it at a red heat with formation of nitride. At dark redness it does not react with gaseous hydrochloric acid, watery vapour, and hydrogen sulphide.

Hydrochloric and sulphuric acids do not attack it, but it reacts with nitric acid in the cold. Melting oxidising agents—*i. e.*, potassium nitrate and chlorate—decompose it at a dark red heat. With the chlorate there ensues a brisk incandescence.

*Analysis.* — Vanadium carbide yielded the folllowing figures :—

|  | 1. | 2. | Theoretical CVa. |
|---|---|---|---|
| Carbon .. .. | 18·39 | 18·42 | 18·98 |
| Vanadium .. | 81·26 | 80·79 | 81·01 |

*Alloys of Vanadium.*—Notwithstanding its high point of fusion, vanadium readily yields alloys, some of which we have studied.

If we heat, in the electric furnace, for three minutes, a mixture of oxide of iron, vanadium anhydride, and sugar charcoal, so as to yield an alloy containing 20 per cent of vanadium (900 ampères and 50 volts), we obtain a homogeneous ingot of a greyish white with a crystalline fracture, and capable of being filed. It contains—

| Iron .. .. .. .. | 72·96 |
|---|---|
| Vanadium .. .. .. | 18·16 |
| Carbon .. .. .. .. | 8·35 |

A mixture of vanadium anhydride, of copper oxide, and of charcoal,—a mixture calculated to yield an alloy containing 5 per cent of vanadium,—yielded, in the electric furnace, a well-fused regulus of a bronze colour, very malleable, capable of being filed with ease, and harder than copper. It contained : — Copper, 96·52; vanadium, 3·38.

We can prepare an alloy of aluminium and vanadium by keeping aluminium in fusion at the bottom of an earthen crucible, and projecting upon the surface of the metal a mixture of vanadic acid and aluminium filings. There ensues a brisk incandescence, and on stirring up the mass we obtain an alloy of aluminium and vanadium very malleable, rather soft, and which if filed clogs the tool. It contains 2·5 per cent of vanadium.

In another experiment we heated, in the electric furnace, a mixture of reduced silver with quantities of vanadic anhydride and of charcoal, calculated for an alloy of 10 per cent. The duration of the heating was three minutes, and the current 900 ampères and 50 volts. We thus obtained a metallic ingot formed of two superimposed layers; on the one part vanadium without a trace of silver, and beneath silver with its fine white colour, which when dissolved gave no reaction of vanadium. These two substances, therefore, have no action upon each other.

*Conclusions.*—On reducing vanadic acid with charcoal in the electric furnace, we can obtain easily and plentifully a cast vanadium containing 4 to 5 per cent of carbon. If the heating is more prolonged we always obtain a new carbide, definite and crystalline, of the formula CV. This compound does not act upon water at ordinary temperatures, and is more stable in presence of acids than in cast vanadium.

At the temperature of the electric furnace, vanadium combines with iron, copper, and aluminium, but it forms no alloy with silver.

From the totality of these properties vanadium approximates more to the non-metals than to the metals. Its carbide approaches the titanium and zirconium carbides which have the same formula.—*Comptes Rendus,* cxxii., p. 1297.

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## ACTION OF MERCURY SALTS ON ALUMINIUM.

### By PERCY A. E. RICHARDS, F.I.C.

Now that aluminium is so extensively used for various instruments, the following reaction that recently came under my notice may perhaps be of general interest :—

A few days ago I was using an aluminium spatula to remove some solid substances from bottles to test-tubes, and having wiped it and laid it on the table, I was surprised to notice that in a couple of minutes the end had become covered with a coating of white powder. I rinsed it thoroughly under water, wiped it dry, and again laid it down. In a very few minutes, however, it was covered as before, and on examining the coating carefully I found it had the appearance of a brush-like " growth " consisting of white filaments standing upright on the flat surface. Whilst watching them they increased visibly, and resembled somewhat the white "*hyphæ*" of *Mucor mucedo.*

A few experiments with the different powders used showed that mercuric iodide was the initial cause of the phenomenon, as this substance produced the same effect when placed on a strip of aluminium. I next tried the action of other solid mercury salts on pieces of this metal under similar conditions, and in each case found that the same " growth " followed. In fact, if the salt was left in contact with the metal for only a minute, and the latter at once wiped or washed, in a short time the brush-like masses of filaments appeared and steadily increased. A

minute globule of mercury also sufficed to start the action. It seems to me that this result is brought about by the mercury first forming an amalgam with the aluminium, and this, reacting at once on the moisture present in the air or on the surface of the metal, forms alumina, at the same time liberating the mercury, which once more forms amalgam. Repeated washing appears to check the action very slightly if once the mercury gets a firm grip on the aluminium.

An approximate determination of the amount of decomposition brought about in a given time was made as follows:—A weighed strip of aluminium was dusted over on both sides with powdered mercuric chloride, and after remaining in contact for a couple of minutes, the latter was washed off and the strip roughly dried. After an hour's interval the metal was again thoroughly washed and dried, and then weighed, when the loss of aluminium had amounted to a little over 8 per cent of the whole. Qualitative analysis of the white filaments showed them to consist, as was supposed, of alumina.

In short, these results show that the greatest care should be taken to prevent any apparatus, &c., of aluminium being brought into contact with mercury in any shape or form.

I have no doubt that other chemists have had similar experiences, and indeed results such as these are only what might be expected considering the powerful action of aluminium amalgam as a reducing agent.

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## ON THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

### By Dr. WYROUBOFF.

SINCE the evening when the periodic classification of the elements was first laid before the Chemical Society by Mr. Newlands, it has been singularly exempt from criticism—unfair, or even severe. Hence we need not be surprised at the discourse of Dr. Wyrouboff. If, remarks Dr. Wyrouboff, the classification of Prof. Mendeleeff had remained what it was at its outset, *i.e.*, a very interesting and highly ingenious table of the analogies and the dissimilarities of the simple bodies, I should never have entertained the idea of discussing it before you.

But M. Mendeleeff has aimed at producing something more and better than a mere *catalogue raisonné* of the elements. He converted his classification into the periodic system. It was a philosophic view, borrowing arguments from the kindred sciences, and imposing itself on us by its universality. He formulated, as the fundamental law of the physico-chemical sciences, the dictum that "all the properties of bodies are periodic functions of their atomic weights."

It would seem that, in view of a question so distinctly put, the first duty of the *savant* must be to intervene, as has been done with particular laws, to check and verify them down to the utmost details. This has not been done —not even dreamt of—and we find, not merely in special researches, but even in works of elementary instruction, the periodic law accepted as a reality beyond all disputes Periodicity being the general and infallible law, the table of Mendeleeff could not err. In works otherwise excellent I have met with the assertion that "no chemical argument could avail against the periodic law."

On reaching this point of its development, the conception of Prof. Mendeleeff becomes essentially injurious. Under pretext of a law which has still to be demonstrated, it forbids us to throw light upon pure matters of observation, and forces us to remain in a vicious circle from which there is no escape. I think that it is time to show clearly that there is nothing which merits the name of *law* or *system*.

I shall consider here merely properties of a purely chemical order, the only ones which chemists have to take into account. Let us take on the one part the atomic weight, and on the other the valence. I say that between these two facts, both constituting chemical attributes absolutely irreducible, we do not see any kind of necessary connection. No known law permits us to conclude that between these two orders of things, absolutely distinct, there is any relation which we may establish without leaving the proper sphere of chemistry. The "periodic law," which claims to establish such a relation, gives us no theoretic antecedent. This by no means implies that it is necessarily false; it signifies merely that it is an empirical law, and as such it is bound to furnish multiple proofs of validity. Among these proofs, without which no empirical law even can acquire the "freedom of the city," it must be demonstrably free from exception. As Mendeleeff puts it :—"The laws of Nature admit no exception ; therefore, the periodic law must be considered as a law of Nature definitely established, which must be accepted or rejected as a whole" ("Elements de Chimie," 1889, 5th Russian edition, p. 465).

A surprising exception is presented by the atomic weight of tellurium. Professor Brauner, who has made a speciality of the art of causing reluctant elements to enter into the classification of Mendeleeff, opens his memoir by laying before us two alternatives: we must either reject the "periodic law," or reject the figure 128 which all authorities have found for the atomic weight of tellurium. But, he continues, as the periodic law cannot be rejected, since it is the truth itself, the value 128 must be inaccurate.

He has therefore submitted tellurium to all the tortures which a substance can undergo. He has melted it, sublimed it, oxidised it, hydrogenised it, dissolved it, and precipitated it, and finally arrived at the result which everybody had reached before him, that the atomic weight varies between the wide limits of 125 and 129.

Hence he concludes that we have here a complex body composed of two elements of very different atomic weights. What are these weights, and what are the distinctive properties of tellurium $\alpha$ and tellurium $\beta$ he does not tell us, for he has not been able to separate them. Still, he takes the number 125 as representing true tellurium, and Prof. Mendeleeff introduces this number in his table, though it has not yet been confirmed by any one.

Prof. Mendeleeff admits for the three cerite metals La $= 138$, Ce $= 140$, and $D_1 = 192$. He required this succession, since cerium yielding a higher oxide could not be placed upon the ascending branch of the curve before lanthanum. But Marignac, Bunsen, Jegel, Rammelsberg, and Wolf have found Ce $= 138$, with deviations not exceeding one or two units of the first decimal. Prof. Brauner alone has obtained 140 by the calcination of the sulphate, a process absolutely defective, as Schützenberger has recently pointed out. As for lanthanum, the majority of recent determinations lead to a figure very near 138·5. Mendeleeff, to give more symmetry to his curve, selected that which presents the lowest figure. As for didymium, it is especially embarrassing for the periodic classification. In 1886 it was split up by Auer von Welsbach into neodymium (Nd $= 141$) and praseodymium (Pr $= 143\cdot6$). Now, this latter gives on calcination an oxide higher than $R_2O_3$, whence neodymium ought to be placed on the same horizontal line as lanthanum. This part of the curve would then become quite irregular, whence Mendeleeff retains in his table of 1889 the old didymium, contenting himself with asserting that the two new metals ought not to be simple bodies, and that there is no occasion to occupy ourselves with them.

The arbitrary selection of oxides and of atomic weights is the gravest critique which we are justified in addressing to Prof. Mendeleeff.

The objections to the "periodic law" urged by Dr. Wyrouboff certainly merit a very careful consideration.— *Les Actualities Chimiques.*

## THE USE OF PHENOLPHTHALEIN IN ILLUSTRATING THE DISSOCIATING ACTION OF WATER.

BY HARRY C. JONES and CHARLES R. ALLEN.

THE fact that an alcoholic solution of phenolphthalein is not coloured red by ammonia or triethylamine, but is so coloured by potassium, sodium, or barium hydroxide, was observed by Menschutkin (*Ber. d. Chem. Ges.*, xvi., 315). He stated that if phenolphthalein is added to alcohol, it does not show an alkaline reaction on the addition of triethylamine or ammonia, and he concluded that the alkalinity of the triethylamine had disappeared, alcohol decomposing the compound of phenolphthalein with tri-ethylamine, even when the latter is present in a large excess.

Without knowing of this work of Menschutkin, we observed facts of the same kind in connection with an investigation which is being carried out in this laboratory by Mr. Mackay. Not only an alcoholic solution of ammonia did not show an alkaline reaction with phenolphthalein, but when a few drops of a water solution of ammonia were added to several c.c. of alcohol, this solution also failed to give an alkaline reaction with alcoholic phenolphthalein. If, however, a considerable volume of water was added to this solution the red colour appeared.

When potassium or sodium hydroxide was substituted for ammonia the red colour appeared at once, without the addition of water, as stated by Menschuthin. There is thus a marked difference between the action of sodium and potassium hydroxides on the one hand, and that of ammonium hydroxide on the other.

It would be difficult to interpret these facts without the aid of the dissociation theory, unless we were content simply to say that potassium and sodium hydroxides are *stronger* bases than ammonium hydroxide, which really explains nothing. This difficulty becomes the more apparent in that Menschutkin was compelled to seek an explanation in the decomposition of the compound of phenolphthalein with triethylamine by alcohol. In the light of the dissociation theory, however, the facts become intelligible.

In a solution prepared by adding a few drops of aqueous ammonia to several c.c. of alcohol, little or no dissociation of the ammonium hydroxide is effected. The addition of water to this solution dissociates the base, the degree of dissociation depending on the amount of water, with respect to alcohol present. The presence of the ions $\overset{+}{NH_4}$ and $\overset{-}{OH}$, into which the ammonium hydroxide dissociates, will cause the phenolphthalein to dissociate into :—

$$CO{<}{}_O^{C_6H_4}{>}\overset{-}{C}{<}_{C_6H_4OH}^{C_6H_4O}+\overset{+}{H}$$

or—

$$CO{<}{}_O^{C_6H_4}{>}\overset{=}{C}{<}_{C_6H_4O}^{C_6H_4O}+\overset{+}{H}+\overset{+}{H}.$$
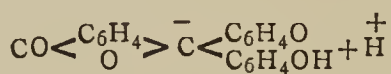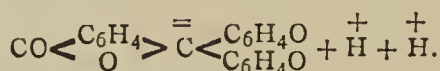
The complex anion is coloured and gives the characteristic colour to the solution in which it is present as an ion. When this coloured anion is combined with the colourless cation, hydrogen, to form a molecule, the solution of these molecules is nearly colourless. When the dissociation of the phenolphthalein indicated above is effected, its cation $\overset{+}{H}$ would combine with the anion $\overset{-}{OH}$ from the ammonium hydroxide, forming water, since these ions cannot, to any appreciable extent, remain uncombined in the presence of each other.

It may be, however, that the actual course of the reaction is slightly different from that above described, in that the ammonium may first combine with the phenolphthalein in the alcoholic solution. The addition of water would then dissociate this compound, liberating the coloured anion referred to above.*

In either case the cause of the colour is the presence of the anion,—

$$CO{<}{}_O^{C_6H_4}{>}\overset{-}{C}{<}_{C_6H_4OH}^{C_6H_4O}$$

or—

$$CO{<}{}_O^{C_6H_4}{>}\overset{=}{C}{<}_{C_6H_4O}^{C_6H_4O},$$
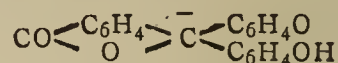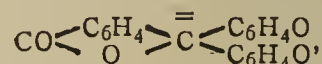
and the dissociation of the compound yielding this coloured anion is effected by the water which is present. The dissociation theory furnishes this explanation. It remains to determine whether the explanation is true. If it is, then a solution formed by adding a little aqueous ammonia to a considerable volume of alcohol should show little or no dissociation, and the amount of dissociation should increase with the addition of water. Solutions of potassium or sodium hydroxide in mixtures of alcohol and water should be more dissociated than corresponding solutions of ammonium hydroxide. Indeed, a solution of sodium or potassium hydroxide in alcohol alone should manifest some dissociation, since, as stated above, it gives the colour reaction with phenolphthalein.

All of these points can be tested experimentally by the conductivity method. We have carried out such measurements as seemed desirable, and give the results in the following tables. Table I. contains the results for ammonium hydroxide. The conductivity of a known volume of a standard solution of aqueous ammonia was at first determined. A measured volume of this solution was then removed, an equal volume of absolute alcohol added, and the conductivity again determined. This process was repeated until nearly all of the water had been removed, the solvent being nearly pure alcohol.

The values under $v$ are the number of litres which would contain a grm.-molecular weight of the ammonium hydroxide at the particular dilution of the solution used. The column $\mu v$ gives the molecular conductivities at the volume $v$ and at 25° C. That portion of the solution which was withdrawn in each case after the conductivity reading had been made, was placed in a Nessler tube, treated with some phenolphthalein, and the strength of the red colour observed approximately. These observations are recorded in the column headed "Colour." No correction is introduced in the results for the conductivity of the water used, since this was tested, and for water which had been re-distilled from acid and alkaline permanganate, was so slight that it is quite negligible.

The corresponding measurements for potassium hydroxide are given in Table II.

### TABLE I.

| $v$. | $\mu v$. | Parts water. | Parts alcohol. | Colour. |
|---|---|---|---|---|
| 11 | 4·8 | 100 | 0 | Strong. |
| 22 | 2·2 | 50 | 50 | Slight. |
| 44 | 1·0 | 25 | 75 | None, or trace. |
| 88 | 1·1 | 12·5 | 87·5 | None. |

### TABLE II.

| $v$. | $\mu v$. | Parts water. | Parts alcohol. | Colour. |
|---|---|---|---|---|
| 8·8 | 214 | 100 | 0 | Strong. |
| 17·6 | 77 | 50 | 50 | ,, |
| 35·2 | 26 | 25 | 75 | ,, |
| 70·4 | 20 | 12·5 | 87·5 | ,, |

The conductivity of a standardised solution of potassium hydroxide in pure alcohol alone, was determined with the following results :—

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* Long (*American Chemical Journal*, xi., 84) has shown that when strong aqueous ammonia is allowed to set on phenolphthalein for a considerable time, phenoldiimidophthalein, a colourless substance is apparently formed. If this compound should be formed to some extent in the alcoholic solutions under discussion, its presence would not affect the colour reactions of the solutions in question, since it is soluble even in alkalis without colour.

| v. | μv. | Colour. |
|---|---|---|
| 8 | 15 | Strong. |

The appearance of the red colour when water is gradually added to an alcoholic solution of phenolphthalein containing ammonia is not sudden. As the results show, it requires the addition of a considerable volume of water before any trace of red can be detected, then a delicate pink colour appears, gradually shading off into red, in the presence of more and more water. This would also be expected, if the colour is a function of the dissociation, since the latter increases gradually with the increase in the water present. The results thus appear to confirm at all points the deductions from the dissociation theory.

This experiment furnishes a very satisfactory lecture demonstration of the dissociating action of water. A few drops of an alcoholic solution of phenolphthalein are placed in a glass cylinder and diluted to, say, 50 c.c., by the addition of alcohol. A few drops of an aqueous solution of ammonia are then added. A red colour may appear where the aqueous ammonia first comes in contact with the alcoholic phenolphthalein, but this will disappear instantly on shaking the cylinder, leaving the solution with a yellowish tint, possibly due to the formation of the ammonium salt of phenolphthalein. Water is then gradually added to the cylinder, when the red colour appears, first faint, then stronger as the amount of water increases. When the red colour has become intense, add a considerable volume of alcohol and the entire colour will disappear, leaving a solution which is slightly yellow. The experiment serves then not only to illustrate the dissociating action of water, but also the driving back of the ions into molecules by alcohol. — *American Chemical Journal*, vol. xviii., No. 5.

## SILICIDE OF CALCIUM.
### By G. de CHALMOT.

WHEN making silicides of different metals in an electric furnace I have often used a flux in order to make the mixture that was used more liquid. In cases where I used lime as a flux, I have often found that the resulting silicide contains considerable amounts of calcium. I have thus introduced calcium in copper, silver, iron, and manganese silicide. I tried to obtain pure calcium silicide by putting into the furnace a mixture of silica, calcium oxide, and carbon. I have found that if these ingredients are mixed in such proportions as to give the compound $CaSi_2$, mainly carbide of calcium is obtained, which, however, contains some silicide. If silica is used in excess, and the amount of carbon is reduced, a calcium silicide of metallic appearance can be obtained, especially if a direct current of low voltage (25 volts and 225 ampères) is used. This silicide often contains some carbide, as can be ascertained by the formation of acetylene gas. It also contains much more silicon and much less calcium than corresponds to the formula $CaSi_2$. All my specimens, moreover, contain some iron. The iron is derived from the furnace, the pencils, and the silica (powdered quartz). All the iron which is present accumulates in silicide, because iron silicide is much more readily formed than calcium silicide.

Different samples contained :—

| | Calculated for $CaSi_2$. | Found. | | | |
|---|---|---|---|---|---|
| | | I. | II. | III. | IV. |
| Si | 58·33 | 71·19 | 62·48 | 81·65 | 91·99 |
| Ca | 41·67 | 19·75 | 28·41 | 15·61 | 5·60 |
| Fe | — | 3·74 | 2·74 | 3·61 | 0·92 |

Specimens I. and II. contain calcium carbide, II. contains lead-coloured crystals imbedded in a more or less

crystalline matter. III. is silver-white, homogeneous, and of crystalline structure. IV. has much the same appearance, but is of darker colour and contains some graphite. It is remarkable that sample IV. was found on the anode, which was the upper pole in this special test. All specimens are hard enough to scratch glass.

The reactions which Wöhler describes (Dammer: *Anorganische Chemie* [2], ii., 327) for calcium silicide, $CaSi_2$, were obtained with all the specimens.

With cold water some hydrogen is formed, more with warm water. Dilute hydrochloric acid forms a yellow silicic acid, and stronger hydrochloric acid forms a more orange-coloured acid. Dilute hydrochloric acid and sulphur dioxide form a red compound. I also found that if hydrochloric acid is brought into contact with finely-divided silicide, hydrogen silicide is sometimes formed, which is self-igniting, and when burning leaves little white flakes of silica.

In these specimens calcium silicide, $CaSi_2$, and silicon are mixed. When they are boiled with hydrochloric acid, the calcium silicide is decomposed and crystals of silicon remain. A part of Sample III., which is apparently homogeneous, was thus treated. The insoluble residue of silicon and silicic acid was washed by decantation, and the silicic acid was dissolved with hot sodium carbonate solution. The remaining black crystals contained Si 95·88, and Fe 4·25 per cent.

This shows that these crystals contain, in addition to silicon, most of the iron silicide which is only a little attacked by boiling hydrochloric acid.

When calcium carbide is heated in an electric furnace with an excess of sand, some crystals are formed, which contain, in addition to silicon, some calcium silicide that can be detected by the hydrochloric acid reaction.— *American Chemical Journal*, vol. xviii., No. 4.

## ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.
### By M. DELAFONTAINE and C. E. LINEBARGER.

EUG. DEMARCAY (*Comptes Rendus*, civ., 111, 1887) states that if the vapour of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la reaction se produit déja, bien qu' avec lenteur à la temperature de la naphthalene bouillante (280°) et avec une extrême rapidité à 440°." (*Loc. cit.*).

Now the chlorides of these rare elements enter into reaction very readily, and may serve as the starting-points for numerous syntheses. Demarcay's statements led us to believe that the reaction in question would furnish a rapid method of obtaining these chlorides in quantity with comparative ease. On making use of the method, however, we found that the reaction does not take place in just the way indicated by Demarcay. We will first communicate our results obtained with niobic acid.

We used niobic pentoxide obtained from re-crystallised potassium oxyfluosalt resulting from treatments of samarskite. The salt was decomposed in the usual way by sulphuric acid, boiled with water, and the residue ignited at strong red heat to expel the last traces of sulphuric acid.

The oxide was placed in one end of a piece of hard glass tubing, constricted in several places (see Fig.), and the tube was heated in the vicinity of the oxide in a combustion furnace to 300°—400°. When the vapour of carbon tetrachloride was passed over the heated oxide, a reaction occurred immediately and a yellowish white sublimate condensed in the cooler parts of the tube. If

the oxide employed was quite pure, almost the totality of it could be converted into the volatile product. By careful application of heat it was possible to drive the sublimed substance into the further portions of the tube; it was then seen that the sublimate could be separated into two main portions, a more volatile one of a yellow colour, and a less volatile one of a nearly white colour. The properties of the yellow product were those of the pentachloride of niobium, while the properties of the whitish portion agreed with those of the oxychloride of niobium. By far the larger portion of the product of the reaction consisted of the oxychloride. The action of carbon tetrachloride on niobic acid seems to yield principally the oxychloride of niobium as the solid product; of the gaseous products formed, phosgene seemed to predominate.

It was thought that possibly the presence of even a slight amount of air might exercise an oxidising influence upon the pentachloride at the moment of its formation, converting it into the oxychloride. We accordingly carried out the same experiment in an atmosphere of carbon dioxide, but could not see that the proportion of the pentachloride was at all increased.

Again it was considered that the relative amount of the pentachloride might be made greater by allowing the reaction to take place in an atmosphere of chlorine; but

chloride is passed into the tube, but the current of carbon dioxide is again sent through it in order to aid in the separation of the pentachloride from the oxychloride of niobium. Any carbon tetrachloride that may have condensed in C D is driven over into E, and B C and C D are so heated that the pentachloride passes through the constriction C and condenses just in front of D. While it is possible to drive almost all of the pentachloride out of B C, and thus to obtain almost pure oxychloride, there is always a not inconsiderable portion of the latter compound that finds its way into C D.

In several experiments we found that a small quantity of an orange-coloured sublimate collected at the further end of C D, which circumstance proves that this substance is more volatile than the pentachloride of niobium. H. Rose (*Ann. Chem. Phys.*, *Pogg.*, xcix., 75, 1856) also observed the formation of such a coloured product when he was engaged in the investigation of chlorine on an intimate mixture of charcoal and tantalic acid. He found that if the acid employed contained " nur die geringste Spur von Wolframsäure, so zeigt sich bei der Darstellung des Chlorids eine sehr kleine Menge von einem rothem Chloride, das etwas flüchtiger als das Tantalchlorid ist." The compound is probably the oxytetrachloride of tungsten, its formation being due to a slight contamination of our niobic acid with a tungsten compound.
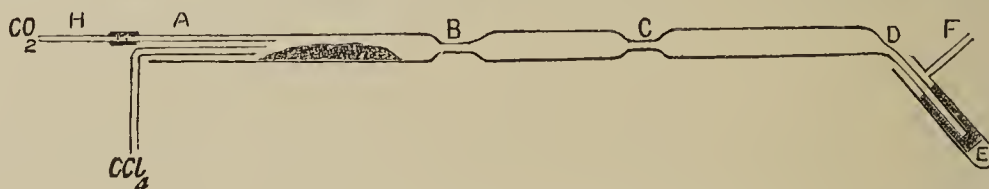


even under such conditions the principal product was found to be the oxychloride.

We conceive, then, that the main reaction of carbon tetrachloride and niobic pentoxide may be represented by the equation—

$$3CCl_4 + Nb_2O_5 = 2NbO.Cl_3 + 3COCl_2,$$
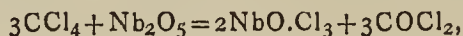
which illustrates again the tendency that niobium has to enter into combination as *niobyl*.

We have prepared a considerable quantity of niobyl chloride according to the above reaction, and, after numerous experiments, have adopted the following method of conducting the operation :—

A tube of the shape indicated in the figure is prepared and filled with niobic pentoxide between A and B. As the chlorine compounds of niobium are quite voluminous, care has to be taken not to employ too much of the oxide; we found that for a tube of about 2 c.m. bore, and having a length of about 40 c.m. between A and B, 10 to 15 grms. could be taken. The tube is placed in a combustion furnace, and the portion in the vicinity of the oxide heated to about 400°. A current of dry carbon dioxide is now passed through the tube to dry it thoroughly and expel the air. The constrictions at B and C are heated nearly to redness to prevent their becoming stopped up, and carbon tetrachloride is gently distilled over upon the niobium compound. It is advisable to discontinue the current of carbonic acid by pinching the delivery tube together at H, since often the pressure of the tube becomes sufficient to throw the acid out of the generator. In the early stages of the operation there occurs a transportation of substance in such a fine state of division that it is carried clear through the tube : in order to prevent its entering the wash-bottle containing sulphuric acid, and connected at F, a little glass wool or asbestos fibre is packed around the end of the tube in E. When B C becomes nearly filled with the products of the reaction, it is heated to a temperature just sufficient to volatilise the pentachloride, which may then be driven over into C D, leaving almost pure oxychloride in B C. When the reaction is at an end, no more carbon tetra-

When we passed the vapour of tetrachloride over tantalic acid, no reaction took place at a lower temperature than 400°, when a small amount of volatile substance was formed, which soon ceased, however. Even on heating to a temperature high enough to cause the Bohemian glass tube to soften, we did not obtain any more of the sublimable product. The tantalic oxid turned yellow and assumed a pasty condition. It is probable that the sublimed substance consisted of the chlorine compounds of niobium, since it is quite possible that our tantalic oxide was not entirely free from an admixture of niobic oxide. This behaviour suggests a method of purification of tantalic acid containing a little niobic acid: we will not lay much stress on this, however, until we have done more work on the subject.

The readiness with which niobium oxychloride was formed in all our experiments contrasting with the comparatively small quantity of the pentachloride obtained illustrates once again the great inclination niobium has to enter into combination, not as an individual element, but in the form of the radical *niobyl*. The action of sulphur and chlorine on NbO, investigated by Delafontaine, the numerous series of oxyfluo-salts prepared by Marignac, and the decomposition of niobyl chloride by magnesium, are other facts of the same import. In this respect the analogy of niobium and vanadium is very striking, but it is almost entirely lacking in niobium and tantalum. — *Journal of the American Chemical Society*, vol. xviii., No. 6.

On the Deep Blue Nitrosodisulphonic Acid.—Paul Sabatier.—Such an acid has never been previously obtained as that which the author has produced by dissolving a small quantity of dry sodium nitrite, which immediately reacts upon sulphuric acid, giving a very intense violet-blue colouration. The blue solutions thus obtained in sulphuric acid are gradually destroyed, but they are nevertheless much more stable than the anhydrous potassium salt of Fremy and Raschig.—*Compt. Rend.*, cxxii., No. 25.

## A MODIFIED AMMONIUM MOLYBDATE SOLUTION.

### By A. L. WINTON.

WHEN phosphoric acid is determined by the molybdate method, it is a common practice to add 15 grms. of ammonium nitrate to the phosphate solution and heat before adding ammonium molybdate. By this means the separation of the yellow precipitate is greatly facilitated and the time of digestion shortened. But to dissolve this nitrate requires some time and very greatly reduces the temperature of the solution, so that special care is necessary in heating it subsequently. In the laboratory of this station it has been our practice to simplify the process by omitting the separate addition of ammonium nitrate and using a molybdic solution containing the requisite quantity of the salt. Such a solution may be prepared according to the following formula:—

I. Dissolve 1000 grms. of molybdic acid in 4160 c.c. of a mixture of 1 part of concentrated ammonia water (sp. gr. 0·90) and 2 parts of water.

Dissolve 5300 grms. of ammonium nitrate in a mixture of 6250 c.c. of concentrated nitric acid (sp. gr. 1·4) and 3090 c.c. of water.

Add I. to II. slowly, with constant stirring. Allow to stand for a few days in a warm place, and decant off the clear liquid.

This solution has the same proportion of ammonium molybdate and free nitric acid as the molybdic solution of Fresenius, but differs from the latter in that *fifty c.c. contain fifteen grms. more of ammonium nitrate.* We have prepared the solution so as to contain this proportion of the salt, because in the routine analysis of fertilisers in the station laboratory 50 c.c. are most commonly employed. This quantity in our experience is usually sufficient for the precipitation of the soluble, insoluble, or total phosphoric acid of mixed fertilisers in solutions representing four-tenths, two, and five-tenths grms. respectively of the material.

In no case ought less than 50 c.c. be used, for otherwise there may not be enough ammonium nitrate present for the perfect separation of the yellow precipitate. When a larger quantity of molybdic solution is required,—as, for example, in the determination of total phosphoric acid in ground bone, bone-black, Thomas slag, &c.,—it may be added without fear that the larger quantity of ammonium nitrate contained in it will in any way interfere with the process. If, however, it is thought desirable, a special molybdic solution containing 15 grms. of added ammonium nitrate to every 75 or 100 c.c. of the liquid may be prepared for such cases.—*Journal of the American Chemical Society*, vol. xviii., No. 5.

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ON THE

## CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION.*

By DOUGLAS McINTOSH,
Physical Laboratory, Dalhousie College, Halifax, N.S.

(Continued from p. 23).

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### Conductivities of the Simple Solutions.

IN order to obtain the data for the calculations it is necessary to draw curves giving the relation of the dilution to the concentration of ions in the simple solutions, and therefore to know the concentrations and conductivities of sufficiently extended series of these solutions. In the case of sodium and potassium chlorides sufficient data were

available for this purpose in Kohlrausch's observations. The following tables give the dilutions and ionic concentrations of solutions of these salts examined by him.

*Potassium Chloride.*

| Dilution. | Concentration of Ions. | Dilution. | Concentration of Ions. |
|---|---|---|---|
| 2 | 0·3861 | 0·400 | 1·7311 |
| 1 | 0·7467 | 0·333 | 2·0328 |
| 0·666 | 1·0885 | 0·285 | 2·3131 |
| 0·500 | 1·4164 | | |

*Sodium Chloride.*

| Dilution. | Concentration of Ions. | Dilution. | Concentration of Ions. |
|---|---|---|---|
| 2·30 | 0·3257* | 0·500 | 1·1738 |
| 2·00 | 0·3689 | 0·400 | 1·3709 |
| 1·80 | 0·4036* | 0·333 | 1·5378 |
| 1·64 | 0·4378* | 0·285 | 1·6776 |
| 1·50 | 0·4732* | 0·250 | 1·7920 |
| 1·20 | 0·5752* | 0·222 | 1·8783 |
| 1·13 | 0·6109 | 0·200 | 1·9320 |
| 1·00 | 0·6777 | 0·182 | 0·9596 |
| 0·666 | 0·9456 | | |

\* Obtained through Prof. MacGregor's interpolation formula, *Trans. N. S. Inst. Sci.*, ix., 112.

In the case of hydrochloric acid sufficient data were not available. I therefore made a series of measurements of the concentrations and conductivities of solutions of this acid, the results of which are given in the following table:—

| Concentration (Grm.-mols. per litre). | Molecular conductivity, ×10⁸. | Concentration (Grm.-mols. per litre). | Molecular conductivity, ×10⁸. |
|---|---|---|---|
| 1·58 | 2550 | 2·80 | 2065 |
| 1·93 | 2403 | 2·88 | 2052 |
| 2·11 | 2347 | 3·15 | 1960 |
| 2·18 | 2305 | 3·29 | 1914 |
| 2·24 | 2290 | 3·39 | 1890 |
| 2·46 | 2245 | 3·60 | 1789 |
| 2·51 | 2192 | 3·83 | 1726 |
| 2·56 | 2164 | 4·13 | 1636 |
| 2·66 | 2141 | 4·55 | 1534 |
| 2·78 | 2090 | 4·87 | 1456 |

The following table contains values of the dilution and concentration of ions in hydrochloric acid solutions, obtained in part by graphical interpolation of the above observations, and in part by the aid of Kohlrausch's tables:—

| Dilution. | Concentration of Ions. | Obtained. |
|---|---|---|
| 2·000 | 0·4310 | Kohlrausch. |
| 1·666 | 0·5090 | ,, |
| 1·428 | 0·5840 | ,, |
| 1·250 | 0·6567 | ,, |
| 1·111 | 0·7269 | ,, |
| 1·000 | 0·7943 | ,, |
| 0·800 | 0·9557 | Observed. |
| 0·666 | 1·1031 | ,, |
| 0·571 | 1·2370 | ,, |
| 0·500 | 1·3600 | ,, |
| 0·444 | 1·4660 | ,, |
| 0·400 | 1·5685 | ,, |
| 0·364 | 1·6516 | ,, |
| 0·333 | 1·7229 | Kohlrausch. |
| 0·286 | 1·8379 | Observed. |
| 0·250 | 1·9132 | ,, |
| 0·222 | 1·9746 | ,, |

The values of the specific molecular conductivity at infinite dilution for potassium chloride, sodium chloride, and hydrochloric acid respectively, were taken to be

$1220 \times 10^{-8}$, $1030 \times 10^{-8}$, and $3500 \times 10^{-8}$ according to Kohlrausch's determination (*Wied. Ann.*, xxvi., p. 204).

(To be continued).

## HYDROFLUORIC ACID.*

### By CARL F. STAHL.

HYDROFLUORIC acid is always made by decomposing ground fluor-spar with sulphuric acid in cast-iron vessels and absorbing the resulting fumes of hydrofluoric acid in leaden vessels of varying construction, containing more or less water, according to the strength desired.

The commercial acid, containing 40 to 52 per cent hydrofluoric, is stored and shipped in lead vessels, or small quantities in gutta-percha bottles. Weaker acid, of about 35 per cent and less, can be stored for a limited time in wood, and is sometimes shipped in barrels, usually oil barrels. In the United States the so-called "chemically pure" acid is packed in ceresine bottles, which answer very well, but must be kept away from the Bunsen burner, as the melting-point of the ceresine is low. In Europe the C.P. acid is shipped either in gutta-percha or platinum bottles, but the acid takes up, in course of time, mineral and organic matter from the gutta-percha and ceases to be C.P. Platinum bottles are the best, but require a heavy investment.

The impurities, which can hardly be avoided in manufacturing commercial hydrofluoric acid, and are therefore always present, are:—

1. *Hydrofluosilicic Acid.*—This is the most important impurity, not because it does any direct harm in the application of the acid, but because the fluorine combined with silica is perfectly useless. The source of the hydrofluosilicic acid is free or combined silica in the fluor-spar, which is all dissolved and volatilised by the hydrofluoric acid. It seems almost impossible to obtain spar free from silica. American ground fluor-spar contains usually about $1\frac{1}{2}$ per cent; samples of English spar which I have tested, were even higher in silica, about 3 per cent; whilst six samples of German spar contained from one-tento to seven-tenths per cent silica. In the rapid determination of silica in fluor-spar, an analytical problem presents itself, which I have not yet solved to my satisfaction. I use the following extremely simple method:—

One grm. of ground fluor-spar. in a platinum dish, with a small platinum spatula, is dried at about 130° C., weighed exactly, moistened with hydrofluoric acid, stirred with a spatula, evaporated to dryness on the water-bath; this is repeated, then dried again at 130° C., and weighed. The difference I assume to be silica, which is only correct when free silica is present, but the spar may contain silicates—for instance, clay; in that case, a fluoride of aluminum would be formed, part of the weight of the silica would be replaced by the weight of the fluorine retained, and the silica be found too low. If carbonates are present the error would not be great, for instance,—

$CaCO_3$ (100) would give $CaF_2$ (78).

and the silica be found too high. The presence of carbonate is, however, easily detected, and the carbonate can be removed with acetic acid. Galena is often present in small quantities and gives the spar a greyish or bluish colour; in that case—

$PbS$ (239) would give $PbF_2$ (245),

an error that would not be perceptible. This simple method, to which any careful boy can be drilled in a short time, is therefore likely to give quite accurate results.

The great damage done by silica in the spar is plainly shown by the following equation :—

$$(1)\ SiO_2 + 3CaF_2 + 3H_2SO_4 = SiF_4(HF)_2 + 3CaSO_4 + 2H_2O$$
$$\phantom{(1)\ }60 \qquad 234 \qquad 294 \qquad 144 \qquad 408 \qquad 36$$
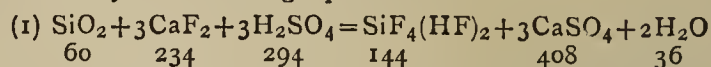
For every part of silica about 4 parts of fluor-spar and 5 parts of sulphuric acid are wasted, or expressing it in money value, for every per cent of silica at least 10 per cent (4 per cent for spar and about 7 per cent for sulphuric acid) should be deducted from the value of the spar.

2. *Sulphuric acid*, which is distilled over in small quantities out of the decomposing vessel, does no harm in the application of the hydrofluoric acid for etching glass or pickling iron. But in analysing the acid it must be determined, otherwise it would be figured as hydrofluoric acid.

On evaporation and calcining, commercial acid should leave but a trace of non-volatile matter.

About five years ago, having made some hydrofluoric acid in an experimental apparatus, I was confronted with the inability to tell what I had made ; that is, I could not find a method which would have enabled me to determine the composition in a reasonably short time.

The method of determining quickly the percentage of a liquid by its specific gravity is of little value for two reasons; first, because the methods for determining the sp. gr. of other liquids can only be used with modifications for hydrofluoric acid, as they involve the use use of a glass instrument of some kind. A glass hydrometer can only be used a few times until the acid has ruined it ; picnometers are out of the question ; even the temperature of hydrofluoric acid cannot be determined directly with a thermometer, as soon as a glass thermometer is placed into the acid the mercury begins to rise from the heat evolved by the action of the acid on the glass. I use, therefore, a platinum hydrometer. A hydrometer made from pure silver would probably last a long time. I have seen one made out of German silver plated with silver, but the hydrofluoric acid got through the plating and ate numerous pinholes into the instrument.

The impurities mentioned above, *i.e.*, hydrofluosilicic acid and sulphuric acid, influence the specific gravity of the hydrofluoric acid to a marked degree, so much that the determination of the specific gravity of an acid of unknown origin is of little value, but for controlling the process in the works, where the character of the raw materials and the degree of purity of the produced hydrofluoric acid is known, it is of value, provided the conclusions drawn from it are from time to time verified by an analysis. It will not do to depend too much on the specific gravity.

Without taking up any time with a description of the experiments, which led finally to the method I use, I will give the latter in detail.

The samples are brought to the laboratory in lead cylinders of convenient size, with a handle. These are placed in water of 15° C., often remaining there for at least five minutes; the specific gravity is taken ; then with the aid of a small platinum tube, serving as a pipette, and chips of filtering paper, to remove a small excess, three portions are weighed out :—

1. Two grms. in a very small platinum crucible (holding about 5 c.c.).
2. Two grms. in a large platinum crucible (holding about 40 c.c.).
3. Four grms. in a small platinum dish.

### A.—*Total Acidity.*

Place the small platinum crucible, covered with its lid, in a large platinum dish (holding about 100 c.c.), then run according to the expected percentage, 25 or 50 c.c. normal caustic solution (40 grms. caustic soda per litre) from a pipette into the dish, upset the covered crucible, and mix the acid and alkali with a platinum stirrer; add 2 drops of a solution of phenolphthalein (1 grm. in 100 c.c. alcohol), and then add more of the normal soda solution from a burette till the colourless liquid assumes the

characteristic bright red colour. Place over a Bunsen burner and heat to about 50° C.; the red colour will disappear. Finally add normal solution from the burette slowly till the red colour remains constant when heated, which indicates that all free sulphuric acid, hydrofluoric acid, and hydrofluosilicic acid have been neutralised. The number of c.c. used we call " *a*."

If litmus is used in place of phenolphthalein, the soda solution has to be added till the colour is perfectly blue, but the end of the reaction is indistinct, while with phenolphthalein as indicator it is very sharp.

### B.—*Hydrofluosilicic Acid.*

To the acid in the large platinum crucible (2 grms.) add 5 c.c. water (measured approximately), then slowly about 2 grms.* potassium carbonate either in small pieces or in concentrated solution, add about 15 c.c. of 50 per cent alcohol, and then as many c.c. of 95 per cent alcohol as water used, which will bring the whole to a volume of about 25 c.c. containing about 50 per cent alcohol ;† let it stand for at least one hour. Filter‡ and wash the gelatinous precipitate, consisting of potassium silicofluoride, with 50 per cent alcohol till blue litmus paper ceases to be turned red by the filtrate. Throw the filter with the precipitate into a platinum dish, add about 25 c.c. of water, and warm to about 50° C.; titrate slowly with normal caustic soda solution and phenolphthalein, as described in the determination of total acidity. The number of c.c. used we call " *b*."

(To be continued).

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxii., No. 25, June 22, 1896.

The Academy proceeded to the nomination of a correspondent for the section of Astronomy, *vice* the late Prof. Cayley. Mr. Gill obtained the unanimity of the votes and was elected.

**Formation of Gaseous and Liquid Hydrocarbides by the Action of Water upon the Metallic Carbides. Classification of Carbides.**—Henri Moissan.

**Letter by Armand Gautier accompanying the Presentation of his Work on the " Animal and Microbian Toxines."**—Toxines are poisons secreted by microbia or formed by the animal economy which, if introduced into our organs or not completely eliminated, bring on a pathological state and involve profound and often permanent modifications of the nutrition and of the vitality of the cellules. These toxines are of three kinds : *a*, The *Ptomaines*, definite alkaloidal poisons formed by the microbia ; *b*. *Leucomaines*, basic substances, definite like the foregoing, but which are formed in our organs themselves in the regular course of life ; *c*. *Toxines, properly so called,* poisons either albumenoid or of an indeterminate chemical nature, playing in general the part of ferments of a surprising activity. They are secreted by pathogenous microbia as well as by venomous animals and by certain plants. They form the essentially injurious portion of venoms and virus. The successive and detailed study of these three orders of poisons forms the principal divisions of this work. Along with the microbian toxines I describe the soluble ferments, animal and vegetable, the specific glandular secretions as well as those curious *antitoxines* which the living organism produces when it reacts and defends itself against the attacks of those dangerous agents. These are the antitoxines now utilised in *seropathy.* At the moment when it was recognised that the direct causes of sickness and of return to health reside in the action of the poisons, ferments, and counterpoisons secreted by the microbia or by the organism itself, it was natural to ask what are the *toxines*, these *ferments*, and these antitoxines, to describe them, and to try to account for their inward nature. This is what I have attempted in the work just published.

**On the X Rays.**—C. Maltézos.—If experiment demonstrates that the refraction of the X rays is not strictly null the radiations are transverse and of an infinitely small small wave-length. These are hyper-ultra-violet rays, and the conclusions of the author's former memoir must be maintained. If, on the contrary, the refraction is absolutely null we may conclude that $\lambda = 0$, for in this case all the optical properties are theoretically demonstrated ; they are terminal radiations. But until this is experimentally demonstrated we must not reject the existence of the hyper-ultra-violet rays. They must exist.

**Procedure of Electrolytic Disargentation of Argentiferous Lead.**—D. Tommasi.—Will be inserted in full.

**Preparation of the Alloys of Aluminium by a Chemical Reaction.**—Charles Combes.—Will be inserted at some length.

**Action of Phosphorus on certain Metallic Chlorides.**—A. Granger.—Nickel and cobalt chlorides behave like ferrous chloride. At a dull red heat phosphorus converts them into nickel and cobalt sesquiphosphides. It is important not to operate at too high a temperature. The sesquiphosphides are not magnetic.

**Measure of a Heat of Etherification by the Action of a Chloride of Acid upon Sodic Alcohol.**—J. Cavalier.—A thermo-chemical paper not suitable for abstraction.

**On Acetal and Monochloric Acetal.**—Paul Rivals.—The substitution of chlorine in aldehyd does not seem to have any appreciable thermic influence upon the formation of the ethylic derivatives of ethyl.

**Ethylic Ethers of the Chloric Acetic Acids.**—Paul Rivals.—A thermo-chemical paper not suitable for abridgment.

**Action of Hydrazines upon the Glyoxylic Acids of the Aromatic Series.**—L. Bouveault.—In order to regulate the decomposition of these glyoxylic acids into aldehyds and carbonic acid the author has sought to transform their carbonyl into a more solid grouping. To this end he has made use of hydrazin.

**Constitution of Inactive Campholenic Acid.**—MM. Guerbet and Béhal.—If we set aside the indications given by oxidation, the formula of camphor, as results from our experiments and as proposed by Bouveault, explains the facts well.

**Rational Denaturation of Alcohol.**—G. Jacquemin.—A single drop of the indifferent sulphuretted oil of Zeiss added to a litre of alcohol at 90° renders it permanently unfit for human consumption. It is the cheapest denaturising agent, cannot be precipitated by any reagent, and does not interfere with any of the industrial applications of alcohol.

**Chemical Mechanism of the Reduction of Nitrates and the Formation of Quaternary Nitrogenous**

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* The amount of potassium carbonate is calculated to neutralise the acids only partly. To avoid an excess it is advisable to test the liquid with litmus paper, which should show a strong acid reaction. But there should be at least enough potash to form potassium silicofluoride with the fluosilicic acid. In analysing acid of entirely unknown composition, I take for every c.c. normal soda solution used for the determination of total acidity 0·05 grm. potassium carbonate. Potassium chloride might be used in place ot the carbonate, but in that case free hydrochloric acid is formed, in which the potassium silicofluoride is somewhat soluble.

† If the liquid contains more than 50 per cent alcohol, potassium fluoride is precipitated; if much less alcohol, potassium silicofluoride may remain in solution.

‡ I use a platinum funnel because glass funnels are acted on, but it does not influence the accuracy of the method.

Matters in Plants.—A. Bach.—Formaldoxime constitutes first quaternary term of the reduction of nitric acid by formic aldehyd.

Nutritive Value of Flours, and on the Economic Consequences of Excessive Sifting.—M. Balland.—A defence of coarse flours.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 1.

Preparation of Strong Solutions of Hydrogen Peroxide. — P. Schiloff (*Journ. Soc. Phys. Chim. Russe de St. Petersburg*, 1893, No. 5).—The author, like Crismer, utilises the solubility of the peroxide in ether. He mixes the commercial product with sodium carbonate until a distinct alkaline reaction is obtained. He filters and shakes up the liquid with 10 to 12 vols. of ether for three to five minutes. The ethereal solution is then lifted off and separated on the water-bath, to expel the chief quantity of ether. The residue is expelled on a paraffin-bath. During these operations but little peroxide is lost. The product obtained contains about half the peroxide present in the original solution. It contains no mineral acid, is not rendered cloudy by silver nitrate, and gives with barium chloride a precipitate perfectly soluble in hydrochloric acid. It is colourless, only has a distinct acid reaction, and has the specific gravity 1·1756. It contains 54 per cent $H_2O_2$. If concentrated to 1·2475, the solution contains 79·57 per cent $H_2O_2$, and has a slight yellowish colour.

Volumetric Determination of Chloroplatinates; Determination of Potassium, Ammonia, Nitrogen, and Platinum. — (*Chemiker Zeitung* and *Comptes Rendus*).

Influence of certain Platinum Metals upon the Accuracy of Results obtained in Quantitation of Gold.

Quantitative Determination of Molybdenum.—C. Friedheim and H. Euler ((*Berichte, Comptes Rendus,* and other Journals).

Volumetric Determination of Molybdenum Trioxide and Vanadium Pentoxide. — Milch, Liebert, Friedheim, Euler, Holverscheit.

A Simplified Method of Determining Phosphoric Acid by means of Molybdic Solution.—J. Hanamann (*Chemiker Zeitung*).—Already inserted.

Detection of Alkaline Perchlorates in presence of Chlorides, Chlorates, and Nitrates. — A. Gooch and Albert Kreider (*Zeit. Anorg. Chemie*).—Already inserted.

An Introduction to the Micro-chemical Analysis of Organic Compounds.—H. Behrens.—No details are given.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1913.

ON THE

## EFFECT OF MOLECULAR BOMBARDMENT ON THE DIAMOND.

### By WILLIAM CROOKES, F.R.S.

IN view of the great interest attaching to the diamond, in consequence of the brilliant researches of M. Moissan on its artificial production, it may be useful to put on record some old observations I made connected with the behaviour of this stone when submitted to molecular bombardment in a vacuum tube under the influence of the secondary current from an induction coil. In 1879[*] I published the fact that diamonds phosphoresced of various colours when treated in the above-mentioned manner, and since that date the phosphorescence of the diamond has been repeatedly exhibited.

During molecular bombardment the diamond becomes discoloured, and in course of time becomes black on the surface.[†] Some diamonds blacken in the course of a few minutes, while others require an hour or more to discolour. This blackening is only superficial, and although no ordinary means of cleaning will remove the discolouration, it goes at once when the stone is polished with diamond powder. Ordinary oxidising reagents have little or no effect in restoring the colour. I consider the following is a reasonable explanation of the phenomenon :—

It is well known that great heat has the effect of converting diamond into graphite. In a paper published in 1891, I showed that in a vacuum tube a silver pole had the appearance of being red-hot, while the volatilisation of the metal proceeded rapidly.[‡] This " red heat " is superficial only. The metal instantly assumes, or loses, the appearance of red heat the moment the current is turned on or off, showing that, if the appearance is really due to a rise of temperature, it does not penetrate much below the surface. The extra activity of the silver molecules necessary to volatilise them is in these experiments confined to the surface only, and is probably less than would be the case with a bad conductor of heat, such as the diamond. In the case of diamond, the electrical and molecular excitation which is capable of raising the superficial layer of silver molecules to redness, heats or excites the outer layer of carbon molecules sufficiently to convert them from diamond to graphite.[§]

I have said the black stain on the diamond is not affected by ordinary oxidising reagents. This would seem to show that it is not due to a layer of amorphous

carbon; but it might be graphite, which is much more resistant to oxidation. Becquerel has shown that graphite is converted into graphitic oxide by long digestion in a warm mixture of potassium chlorate and strong nitric acid, while diamond—even in a very finely-powdered state—is absolutely unaffected by the mixture.[*] I accordingly tried the following experiment :—Three diamonds of a good white colour, and approximately of the same size, were selected from a parcel I brought from the Kimberley Mine in April last. One was set aside for comparison, while the other two were bombarded in a vacuum tube for five hours. At the end of that time they were well blackened superficially. One of these discoloured stones was also set aside for comparison, while the other was digested for three days in a mixture of potassium chlorate and strong nitric acid at a temperature of about 50° C. An exactly similar experiment was performed with three bright yellow diamonds from the Wesselton Mine, Kimberley.

At the end of the three days' digestion the reagent was washed away and the diamonds examined. Not only was the superficial blackening entirely removed, but on comparing the cleaned diamonds with the original ones which had been at first set aside, they had, if anything, appreciably more brilliancy. This proves that the black stain on the surface is produced by the conversion of the superficial layers of molecules from diamond to graphite. Microscopic examination under high powers fails to show any alteration of the smooth crystalline surface either before or after the blackened diamonds have been treated to the chemical reagents.

It is not necessary to expose the diamond in a vacuum to electrical excitement in order to produce a change. Some diamonds phosphoresce when exposed to the sun's rays or to an electrical discharge in the air, and many more are phosphorescent when exposed to the Röntgen rays. In the latter cases a slight superficial blackening also takes place.

On recently examining some diamonds sealed up in a vacuum tube and considerably blackened many years ago, I am inclined to think that they are by no means so dark as they were when they were being frequently exhibited. It is not beyond credibility that a renovation may take place in the course of time and rest. The molecules of diamond are in a state of constant motion. Those constituting the body of the diamond vibrate in a manner different to the converted graphite molecules forming the superficial layers. It is not so very unlikely that the whole mass of crystalline diamond vibrating in one manner may so hamper the movement of the comparatively infinitesimal number of graphite molecules vibrating in another direction that the latter may gradually be constrained to take on themselves the same kind of motion as the crystal itself is engaged in, and so become ultimately re-converted from graphite to diamond.

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* " Most of these gems (diamonds), whether cut or in the rough, when coming from the South African fields, phosphoresce of a brilliant bright blue colour. Diamonds from other localities shine with different colours, such as bright blue, pale blue, apricot, red, yellowish green, orange, and bright green. One beautiful green diamond in my collection, when phosphorescing in a good vacuum, gives almost as much light as a candle; the light is pale green—almost white. A beautiful collection of diamond crystals, kindly lent me by Professor Maskelyne, phosphoresces with nearly all the colours of the rainbow, the different faces glowing with different shades of colour."—*Phil. Trans.*, Part II., 1879, p. 660.

† *Phil. Trans.*, Part II., 1879, p. 658. par. 625.

‡ *Proc. R. S.*, vol. l., p. 99, June, 1891, " On Electrical Evaporation."

§ In other cases, also, long-continued molecular bombardment has the effect of profoundly altering the physical state of an amorphous powder. Some chemically pure alumina sealed up in a vacuum tube in 1879 was originally snow white; but after being frequently submitted to the molecular discharge for the purpose of exhibiting its brilliant phosphorescence, it gradually assumed a pink tinge, and on spectroscopic examination in sunlight a trace of the crimson alumina line could be seen. The repeated molecular excitation has slowly converted the amorphous powder to a crystalline form.

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## ON THE BEHAVIOUR OF RÖNTGEN'S RAYS.

### By C. DOELTER.

THE behaviour of Röntgen rays with minerals has been carefully examined by the author, with especial reference to their density and chemical composition. The Röntgen rays are especially important as a means for distinguishing precious stones from doublets. The transmissibility of a mineral for the Röntgen rays is not connected with its density; only the very heavy species (above 5) being non-transmissive. Among light minerals, rock-salt, sulphur, potash, saltpetre, and realgar are non-transmissive; among heavy minerals, cryolite, corundum, and diamond are quite transmissive. In many silicates the introduction of iron in place of aluminium occasions non-trans-

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* *Ann. de Chim. et de Phys.*, 4, xix., p. 392.

missiveness, whilst compounds of boron and aluminium are more transmissive, and arseniates and phosphates keep back the rays. A general dependence on chemical composition can no more be shown than on molecular weight and on density. Dimorphous minerals show, for the most part, scarcely perceptible differences in transmissibility, only such differences are more perceptible in rutile and brookite, pyrites and marcasite, calc-spar and arragonite. If the rays are thrown through crystals in different crystallographic directions, the differences observed were unimportant, as in andalusite, diamond, and quartz. Among the transmissive minerals rank diamond, boric acid, amber, corundum, meerschaum, kaolin, asbestos, and cryolite; among the non-transmissive are epidote, cerussite, baryta, pyrites, arsenite, rutile, valentinite, and almandine. The author recognises eight groups the several members of which showed little difference in transmissiveness, though they differed strongly from each other :—(1) Diamond ; (2) corundum ; (3) talc ; (4) quartz ; (5) rock-salt ; (6) calc-spar ; (7) cerussite ; (8) realgar.—*Mittheil. d. Naturw. Vereins für Steiermark,* 1895, and *Chemiker Zeitung.*

## PROCEDURE FOR ELECTROLYTIC DESILVERING ARGENTIFEROUS LEAD.

### By D. TOMMASI.

THE principle on which this procedure is founded consists in electrolysing a lead solution which not merely possesses an extremely weak electric resistance, but does not give rise to lead peroxide (PbO₂), and, in taking the argentiferous alloy itself as anode and as kathode, a metallic disc which cannot be attacked by the bath.

Under the action of the current the lead of the anodes enters into solution, and is transferred, in the state of spongy crystals, upon the disc which serves as kathode, whilst all the silver contained in the lead, being insoluble in the bath, is deposited at the bottom of the vat in a perforated receiver destined for its collection.

The following is the course to be followed for the electrolytic extraction of silver from argentiferous lead :—

We melt the lead, and then cast it in moulds having the shape and the thickness which is intended for the anodes. This being done, we suspend each anode to one of the two metallic poles which are found placed about the upper part of electrolyser.

Each metal pole is fitted with an endless screw and with nuts. At the ends of these poles are fixed plugs intended to connect the anodes electrically among themselves, and to secure the whole to the positive pole of the dynamo.

The object of this arrangement is not merely to keep the electrodes at a determined distance from each other, but to approximate them if this distance becomes too great in consequence of the progressive wear of the anodes.

The disc which serves as kathode is placed between the two anodes, and communicates with the negative pole of the dynamo by means of a metal brush rubbing upon its axle.

The electrolyser being fitted up we pour in the bath (a solution of the double acetate of lead and sodium or of lead and potassium), close the circuit, and cause the disc to revolve at the rate of one or two rotations per minute.

When the current is established, the lead begins to deposit upon the disc in the form of small spongy crystals. When the deposit of lead has acquired a sufficient thickness, and it is thought suitable to remove it, the current is interrupted and the scrapers closed.

In consequence of their friction against the faces of the disc, the lead is detached and falls into sloping gutters, which bring it upon a sieve of metal cloth. The lead is drained, washed with distilled water, and then submitted to a strong pressure.

The liquid which flows off is added to the washing-waters, and the whole evaporated down to 30° Baumé. When cold, this liquid is introduced into the electrolysers by means of a pump. The compressed lead is heated on a crucible with 2 to 3 per cent of charcoal in powder, and when melted it is cast in ingots.

When the anodes are dissolved, we may either replace them with fresh anodes, or merely withdraw the silver deposited at the bottom of the vat. In this latter case we raise the disc by means of a windlass; then withdraw the perforated recipient placed at the bottom of the vat at the beginning of the operation; this contains all the silver left behind by the argentiferous lead of the anodes.

The silver, when collected, washed, and dried, is melted in a crucible with sodium nitrate and a little borax, and is then cast in ingots.—*Comptes Rendus,* cxxii., p. 1476.

## THE DETECTION OF MERCURY IN CASES OF POISONING.

### By D. VITALI.

THE recognition of mercury, in general rather easy, may yet become doubtful if the poison is only present in fractions of m.grms. In such cases the expert should content himself with carrying out one or two of the most characteristic reactions.

After the destruction of the organic matter, according to the Fresenius-Babo method, the filtrate is evaporated as far as possible without separating potassium chloride or the supposed potassium mercury chloride in crystals. A current of sulphuretted hydrogen is passed for a rather long time through the solution, which is then allowed to stand for some hours in a moderately warm place. The mercury sulphide, after settling, is repeatedly washed by decantation, then dried in a porcelain capsule on the water-bath, and dissolved in *aqua-regia.* The solution is freed from free chlorine and nitric acid by evaporation with the addition of hydrochloric acid. The residue consists of mercuric chloride, and is decomposed electrolytically. In place of the methods of Smithson, of Danger and Flandin, or Mayençon (which have been hitherto used, but are not sufficiently sensitive, often erroneous or too tedious), the following procedure may be successfully used :—

The supposed solution of mercury is put in a minute porcelain capsule, in which are immersed small pieces of sheet-gold and small iron tacks. The mercury present in solution deposits itself upon the gold, and, according to the author's experiments, partly upon the iron nails. After about an hour, when the deposition of the mercury is probably complete (which may be easily ascertained by testing a drop with a drop of sulphuretted hydrogen water), the fragments of the two metals are removed from the liquid, washed with water, dried with filter-paper, and heated to faint redness in a test-tube about 6 c.m. in length and 6 m.m. in width. The mercury forms a grey coating near the heated part of the glass. The fragments of gold and the iron nails are then taken out; a crystal of iodine is put into the tube, which is gently heated. The iodine vapours in contact with the mercurial coating form at first a yellow ring, passing into red (mercuric) iodide. If the iodine is used in excess there is formed a brown ring. By this process 0·00001 grm. of mercury can be recognised.

The mercury deposited on the metals may also be shown by placing the washed and dried portions of gold and iron in a porcelain capsule, covered with a small inverted porcelain capsule moistened with solution of gold chloride, heating the lower capsule then on the water-bath. However minute a quantity of mercury has been attached to

the metals, the inner surface of the upper capsule displays a violet-blue colour, owing to the reduction of gold occasioned by the mercurial vapours.—*Chemiker Zeitung.*

# ON THE SPECTRUM OF PHOSPHORUS IN FUSED SALTS, AND ON CERTAIN METALLURGICAL PRODUCTS.

### By A. DE GRAMONT.

THE fused phosphates, submitted to the action of the condensed spark according to the arrangement which I have already employed for other salts (*Comptes Rendus*, July 8, 1895, and June 8, 1896) give a very beautiful spectrum of the lines of phosphorus, easy to obtain, and superior in definiteness and in luminous intensity to that of the Plücker phosphorus tubes. I have thus resumed the study of the spectrum of this element, formerly undertaken by M. Salet, with a less dispersion and in different conditions, an explanation of which will be found in the author's "Traité de Spectroscopie."

I have principally made use of melted sodium phosphate and potassium phosphate; and on cutting off from the spectrum given by these salts the sodium and potassium rays mentioned in a former memoir (*Comptes Rendus*, June 15, 1896), I have obtained the following wave-lengths for the line spectrum of phosphorus :—

|   |   |   |
|---|---|---|
| | 650·6 | Diffused. |
| | 645·8 | Well-marked. |
| | 608·8 | Quite visible ; not seen by Salet. |
| | 604·2 | Strong, bright. |
| α. | 603·45 | Rather strong, fine. |
| | 602·5 | Strong, bright. |
| β. | 549·85 | Quite well visible. |
| | 546·2 | Feeble |
| | 545·3 | Feeble. |
| γ. | 542·35 | Very strong. |
| | 540·9 | Strong ; not seen by Salet. |
| | 538·5 | Strong ; not seen by Salet. |
| | 534·0 | Strong, rather diffused ; not seen by Salet. |
| | 531·1 | Strong. |
| | 529·2 | Strong. |
| δ. | 525·0 | Very strong. |
| | 496·8 | Very well visible, diffused ; not seen by Salet. |
| | 494·1 | Well-marked. |
| ε. | 460·3 | Very strong. |
| | 458·85 | Very strong. |

The alphabetical designations of the rays are those of Salet.

There is little difference of intensity between the rays marked as *strong* and those marked *very strong*.

The rays most easily recognised, from their position and their aspect, are—the triplet P α in the red and the doublet P ε in the blue, and then the green rays from P γ to Pδ. Three of the latter have not been seen by Salet, but they correspond in intensity and nearly in position with the lines appearing on a plate of Plücker's memoir, from which their wave-length has been approximately reduced by Watts. Besides, the spectra published by Plücker, and then by Salet, had been produced by tubes containing either vapour of phosphorus at a reduced pressure, or phosphorus chloride from which the rays of chlorine had been eliminated, therefore in conditions differing as to pressure and temperature.

The spectrum of phosphorus which I have just given is not peculiar to the melted salts. I have recognised it also, in the cold, in phosphoretted metallurgical products, which, having been submitted to direct spectral examination in the condensed spark with my arrangement for the

study of minerals ("Analyse Spectrale Directe des Mineraux": Paris, 1895), show easily, among the rays of the metal, those also of phosphorus. These latter are especially visible and brilliant in the copper phosphides, where the metallic rays are not very numerous. In phosphoretted cast-irons the multiplicity of the rays of iron would render the recognition of those of phosphorus more difficult if the triplet P α did not stand out very brightly in the red. This effect has been very characteristic and persistent in a cast-iron containing 2 per cent of phosphorus courteously sent me by M. Meyer, manager of the works of Dudelange (Luxembourg). An iron phosphide, extracted by M. Friedel from the meteorite of the Cañon Diablo, has also yielded the principal rays of phosphorus. I have since pursued the research for the latter in the cast-irons analysed at the Assay Office of the Ecole des Mines, kindly placed at my disposal by M. Adolphe Carnot. I have found that the presence of the triplet P α, more and more transient with the decrease of the proportion of phosphorus in the metal, became almost invisible within limits comprised between one-hundredth and one-thousandth.

For other non-metals, also, it seems to me that the duration of the appearance of their spectrum in metallic compounds, minerals, or fused salts is, if not proportional to the quantity of the non-metal, at least a function of the latter. Perhaps we may here find a basis for new attempts in spectral quantitative analysis. — *Comptes Rendus*, cxxii., p. 1534.

# LONDON WATER SUPPLY.

### REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1896.

### By WILLIAM CROOKES, F.R.S., and PROFESSOR DEWAR, F.R.S.

*To* MAJOR-GENERAL A. DE COURCY SCOTT, R.E., *Water Examiner, Metropolis Water Act,* 1871.

London, July 11th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

The rainfall at Oxford during the month of June shows an excess of 0·31 inch, the total actual fall being 2·42 inches (occurring on ten days only), whereas the thirty years' average fall is only 2·11 inches.

Of this amount of rain 1·94 inches fell from the 4th to the 10th, inclusive.

There is still a large deficiency of rain for the year, viz., 4·38 inches.

Our bacteriological examinations gave the following results :—

|  | Colonies per c.c. |
|---|---|
| Thames water, unfiltered .. .. .. .. .. | 2081 |
| Thames water, from the clear water wells of the five Thames-derived supplies.. highest | 70 |
| Ditto     ditto     .. .. .. .. lowest | 2 |
| Ditto     ditto     .. (12 samples) mean | 32 |
| New River water, unfiltered .. .. .. .. | 836 |
| New River water, from the Company's clear water well .. .. .. .. .. .. .. | 35 |
| River Lea water, unfiltered    .. .. .. .. | 1729 |
| River Lea water from the East London Company's clear water well .. .. .. .. .. | 28 |

A comparison of our figures shows that, in spite of the sudden excess of rain after a prolonged drought, the Companies have effectively coped with the additional amount of extraneous matter brought down by the flood waters.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

# A STUDY OF THE ZIRCONATES.*

### By F. P. VENABLE and THOMAS CLARKE.

THIS class of compounds of zirconium has received but little attention from chemists. The chief investigator in the past who has worked in this field was Hiortdahl (*Ann. Chem. Pharm.*, cxxxvii., 34, 236). Of recent years several papers by L. Ouvrard (*Comptes Rendus*, cxii., 1444-46, and cxiii., 1021-22) have appeared. The accounts given in the various text-books of these zirconates are based upon the work of Hiortdahl, or upon such abstracts of it as were to be found in the *Jahresberichte*, or in such dictionaries as that of Watts. This is unfortunate, as to the best of our knowledge the work of Hiortdahl itself is in some respects inaccurate and erroneous, and the abstracts of it are misleading. Before giving an account of our own experiments, it may be well to gather together the statements regarding these bodies as given by Watts and in the original article of Hiortdahl.

Watts says that the compounds of zirconia with the stronger bases are obtained by precipitating a zirconium salt with potash or soda, also by igniting zirconia with an alkaline hydroxide. "Zirconate of potassium thus obtained dissolves completely in water." His first mode of preparing the zirconates is very questionable; the last statement is not true. He then goes on and describes zirconates of sodium, calcium, and magnesium, as described by Hiortdahl. The details of Hiortdahl's analyses, &c., will show on what an imperfect basis the knowledge of the constitution of these bodies rests. Hiortdahl states that he secured direct union only by ignition with alkaline carbonates. His attempts with the volatile chlorides failed. On heating zirconia with sodium carbonate one equivalent of carbon dioxide was driven out, and it is on the loss of carbon dioxide upon ignition that his figures for the composition of the resulting products are largely based. On heating equivalent amounts of zirconia and sodium carbonate a crystalline mass was obtained, which slowly absorbed moisture from the air. On treating this with water no decomposition was noted at first, but soon the water became alkaline and zirconia separated. This was taken as proof that the zirconia was decomposed by the water. In the experiment 0·3910 grm. zirconia heated with 0·3130 grm. sodium carbonate to a dark redness for nine hours lost 0·1310 grm. carbon dioxide, and on treatment with water 0·3871 grm. "zirconia," or 99·03 per cent was left. If an

* From the *Journal of the American Chemical Society*, xviii., No. 5.

excess of sodium carbonate is used one can drive out two equivalents of carbon dioxide. A little further down he notes that the "Gewichtsverlust zugleich von der Temperatur und der Dauer des Glühens abhängt." These are the determinations from which formulæ for the zirconates are worked out.

It is scarcely necessary to say that for purposes of calculation these figures are entirely worthless. The loss of carbon dioxide is due to a partial formation of hydroxide as well as to a combination with zirconia. The fused mass of sodium carbonate, hydroxide, zirconate, and unchanged zirconia will of course prove hygroscopic, and water will wash away all except the last two mentioned. We have failed to get any positive evidence that a zirconate formed by fusion was decomposed by water or was appreciably soluble in it.

In his second paper, Hiortdahl treats the fused mass of zirconia and sodium carbonate with water acidified with hydrochloric acid, and analyses the residue, finding in it —$ZrO_2$, 78·54 per cent; $Na_2O$, 5·40 per cent; and $H_2O$, 16·89 per cent; corresponding to $Na_2O.8ZrO_2$. He gets the zirconate of magnesium and calcium by fusing zirconia and silica with magnesium chloride and calcium chloride respectively.

Ouvrard obtained his zirconates by fusions with the chlorides, also using those of lithium, calcium, strontium, and barium. In some cases, instead of using zirconia, he took powdered zircons, obtaining silico-zirconates.

In our own experiments the following methods of forming the zirconates were tried :—

I. Fusing in boron trioxide, the zirconia and the basic oxide (Ebelmen).
II. Fusing zirconia with alkaline carbonates (Hiortdahl).
III. Fusing zirconia with alkaline hydroxides.
IV. Fusing zirconia with alkaline or earthy chlorides (Hiortdahl).
V. Precipitation of solutions of zirconium salts with alkaline hydroxides (Watts).
VI. Dissolving zirconium hydroxide in strong solutions of sodium or potassium hydroxide, and precipitation by dilution or by neutralisation with an acid.

### I. *Fusion with Boron Trioxide.*

This method, made use of by Ebelmen in the case of other oxides, is useless in the case of zirconia, because this oxide is not taken up by the boron trioxide, and so does not come in contact with the other oxide. The melt of boron trioxide was kept at a high temperature for a number of hours without any appreciable solvent action upon the zirconia, added in small portions.

### II. *Fusion of Zirconia with Alkaline Carbonates.*

The purified zirconia used had been dried at the temperature of the steam-bath, and therefore was not in the inactive condition brought about by igniting it at a very high temperature. This was the case in the subsequent experiments also.

It is by fusion with sodium carbonate that Hiortdahl claimed to have prepared his zirconates. Ouvrard seems to have gotten little besides crystals of zirconia. Very little action could be seen in the experiments described below. The zirconia sank to the bottom of the fused mass, and remained without apparent change for hours. Varying the time of heating did not seem to have much effect upon the results.

After the fused mass had cooled it was leached with successive portions of water until no alkali could be detected. The wash water contained no zirconium. As the mass left will absorb carbon dioxide, it was dried as rapidly as possible at about 150° to constant weight. Dilute hydrochloric acid was used to separate the zirconate formed from the unchanged zirconia. As this zirconia was now in the ignited and even crystalline form,

it was concluded that it was insoluble in the dilute acid. The zirconia in the solution was precipitated as hydroxide and determined as oxide, and the alkali determined in the filtrate. Two grms. of zirconia were used in each case, and a large excess of the carbonate. The amount of unattacked zirconia ranged from 93 to 99 per cent, showing thus very little action after many hours of fusion. In some cases, therefore, the amount of supposed zirconate obtained was too small for reliable analysis.

### A. *With Sodium Carbonate.*

Three experiments with sodium carbonate were carried to completion :—

1. Two grms. zirconia and 8 grms. sodium carbonate were fused three hours. Amount of residue after leaching, soluble in dilute hydrochloric acid, 0·1588 grm., or 8 per cent. In this $ZrO_2 = 75\cdot70$ per cent; $Na_2O = 24\cdot30$.

2. Two grms. zirconia fused with 16 grms. sodium carbonate for four hours. Amount of residue soluble in hydrochloric acid, 0·3042 grm. Percentages: $ZrO_2$, 74·18; $Na_2O$, 25·81. These correspond fairly with $(ZrO_2)_3(Na_2O)_2$.

3. Two grms. zirconia fused with 16 grms. sodium carbonate for eight hours. Amount soluble in dilute hydrochloric acid, 0·1220 grm., or 6 per cent. Percentages: $ZrO_2$, 58·16; $Na_2O$, 41·84.

### B. *With Potassium Carbonate.*

When potassium carbonate was used the action was so slight that it was not possible to get enough for analysis. In one case, after heating for ten hours, the amount soluble was just one-half per cent. This accords with the observation of Ouvrard.

Of course it is possible that the leaching with water had a partially decomposing effect upon the zirconates. Very little could be justly concluded, however, from experiments in which there was so little action, therefore the effort at forming the zirconates by fusion with the carbonates was abandoned.

### III. *Fusion of Zirconia with Hydroxides.*

1. *Fusion with Sodium Hydroxide.*—Here considerable action was noticed. The fusions were made in a silver dish. The heating was kept up until the mass became semi-solid. The treatment of the fused mass and the analysis were carried out as before. No zirconium was detected in the wash water.

1. Two grms. zirconia fused with 8 grms. sodium hydroxide. Total amount dissolved, 1·1855 grms. An analysis, reduced to dry basis, gave $ZrO_2$, 92·29, and $Na_2O$, 7·65.

2. Same amount taken as in Experiment 1. Total amount dissolved, 0·7655 grm., containing $ZrO_2$, 93·19, and $Na_2O$, 6·22.

3. Two grms. zirconia and 16 grms. sodium hydroxide. Amount dissolved, 0·8004 grm., containing $ZrO_2$, 92·57, and $Na_2O$, 7·38.

4. Two grms. zirconia were fused with 8 grms. of sodium dioxide, instead of the hydroxide. Amount dissolved, 0·7074 grm., and this contained 91·21 per cent $ZrO_2$.

$Na_2O.(ZrO_2)_6$ contains $ZrO_2$, 92·20, and $Na_2O$, 7·80. $Na_2O.(ZrO_2)_7$ contains $ZrO_2$, 93·29, and $Na_2O$, 6·76.

2. *Fusion with Potassium Hydroxide.* — These were carried out in a manner similar to those with sodium hydroxide, and the action seemed to be about the same. In each experiment 2 grms. of zirconia were taken and fused with 16 grms. of potassium hydroxide.

1. Dissolved by hydrochloric acid 0·8850 grm., which contained 79·63 per cent $ZrO_2$.

2. Dissolved 1·5241 grms., which contained $ZrO_2$, 82·98; $K_2O$, 17·00.

3. Dissolved 1·2078 grms., which contained $ZrO_2$, 78·59; $K_2O$, 21·40.

4. Dissolved 0·9297 grm., which contained $ZrO_2$, 85·51; $K_2O$, 14·49.

In analysing these alkaline zirconates the water present was not determined. The moist powder was treated with hydrochloric acid, the insoluble portion caught upon a filter, and the zirconia and alkali determined in the filtrate and the results calculated upon a dry basis. If the analysis given by Hiortdahl is calculated upon a dry basis, it gives for $ZrO_2$, 93·51, and $Na_9O$, 6·49, or very nearly the numbers gotten in Experiment 2 in the fusions with sodium hydroxide.

It is difficult to interpret the results of these fusions with the alkaline carbonates and hydroxides. The fusions do not yield the same definite results each time, and indeed it cannot be claimed from the analyses that definite zirconates have been prepared. Some allowance must be made for the imperfect method of separation of the zirconate from the unchanged zirconia, some of the former being taken up by prolonged digestion with hydrochloric acid. There is a marked tendency, however, toward the formation of certain zirconates under approximately the same conditions. Two of the experiments with sodium carbonate give results fairly in accordance with the formula $(Na_2O)_2(ZrO_2)_3$. In the fusion with sodium hydroxide the results range from $(Na_2O)(ZrO)_5$ [$ZrO_2 = 90\cdot76$; $Na_2O = 9\cdot24$], to $(Na_2O)(ZrO)_8$ [$ZrO_2 = 94\cdot08$; $Na_2O = 5\cdot92$], and it is with these that the analysis of Hiortdahl agrees, though his was a fusion with sodium carbonate. Why there should be this difference is not very clear. The tendency is manifestly toward the formation of what may be called the polyzirconates, having a considerable excess of zirconic acid. In the case of potassium the carbonate failed to give a compound. The hydroxide gives results ranging from $(K_2O)(ZrO_2)_3$ [$ZrO_2 = 79\cdot57$; $K_2O = 20\cdot43$], to $(ZrO_2)_5(K_2O)$, [$ZrO_2 = 86\cdot74$; $K_2O = 13\cdot26$]; again polyzirconates with excess of zirconia.

Other fusions were carried out with sodium and potassium hydroxides, and the resulting masses were leached with dilute acetic acid, a solvent which had to be used in leaching away the alkaline earths in the subsequent experiments. In the case of sodium the leaching removed practically all of the alkali. In the case of potassium a substance containing $ZrO_2$, 78·59 per cent, and $K_2O$, 21·41 per cent, was left. This nearly corresponds to the formula $K_2O.(ZrO_2)_3$. It is almost exactly the result gotten in one of the previous experiments.

3. Lithium gave no zirconate when the carbonate was used for the fusion. With the hydroxide it gave the following results :—

Two grms. $ZrO_2$ were fused with excess of lithium hydroxide, leached with dilute acetic acid and with water. This gave on analysis $ZrO_2$, 89·11 per cent; $Li_2O$, 10·99 per cent. Percentage of $ZrO_2$, calculated for $Li_2O.2ZrO_2$, is 89·13.

4. Calcium oxide was also heated for a number of hours with zirconia, and gave the following results :—

| | I. | II. | Calculated for $CaO.ZrO_2$. |
|---|---|---|---|
| $ZrO_2$ .. .. | 70·11 | 70·83 | 68·54 |
| CaO .. .. | 29·88 | 29·14 | 31·46 |

These residues, after treatment with dilute acetic acid and water, were crystalline.

5. Barium hydroxide differs from that of calcium in that it fuses readily, and thus affords much better opportunity for reaction. The fusion gave abundant evidence of action. The excess of hydroxide was washed out with water. The carbonate present was dissolved away with dilute acetic acid until there was no more barium in the wash water. No zirconia was found in any of these washings. Towards the latter part of the washing the solid particles settled out with great difficulty. The residue was analysed with the following result :—

| | Found. | Calculated for $BaO ZrO_2$. |
|---|---|---|
| $ZrO_2$.. .. .. | 55·51 | 55·95 |
| BaO .. .. .. | 44·49 | 44·05 |

This is a greyish white powder, very fine, and easily soluble in hydrochloric acid. Practically all of the zirconia was taken up, leaving little undissolved by the hydrochloric acid.

6. Strontium oxide was prepared by ignition of the nitrate, and heated in the same way as the calcium oxide. This mass was pinkish white, probably from slight impurities, and was completely soluble in dilute hydrochloric acid. On analysis the following results were obtained :—

|  | Found. | Calculated for SrO.ZrO₂, |
|---|---|---|
| $ZrO_2$.. .. .. | 54·22 | 54·55 |
| $SrO$ .. .. .. | 45·77 | 45·45 |

7. The magnesia (8 grms.) and zirconia (2 grms.) were heated together for about four hours, and then treated in the same manner as the calcium fusion, *i. e.*, first leached with dilute acetic acid, and then washed with water until free from magnesia. The residue gave evidence of being crystalline :—

|  | Found. | Calculated for MgO.ZrO₂. |
|---|---|---|
| $ZrO_2$.. .. .. | 76·28 | 75·30 |
| $MgO$.. .. .. | 23·70 | 24·70 |

(To be continued).

## CALCULATION OF THE CONDUCTIVITY OF MIXTURES OF ELECTROLYTES HAVING A COMMON ION.*

By DOUGLAS McINTOSH, Physical Laboratory, Dalhousie College, Halifax, N.S.

(Concluded from p. 36).

### Results of Observations on Mixtures.

#### (A).—Sodium and Potassium Chlorides.

THE following series of mixtures of potassium and sodium chloride solutions were examined :—

| Concentration (Grm.-mols. per litre). | | Conductivity, ×10⁸. |
|---|---|---|
| KCl. | NaCl. | |
| 3·88 | 5·12 | 2494 |
| 3·20 | ,, | 2326 |
| 2·49 | ,, | 2187 |
| 1·93 | ,, | 2029 |
| 3·88 | 5·12 | 2494 |
| ,, | 4·28 | 2404 |
| ,, | 3·37 | 2316 |
| ,, | 2·56 | 2196 |
| ,, | 2·06 | 2124 |
| 3·46 | 3·20 | 2160 |
| 3·80 | 2·23 | 1877 |

Table A contains a statement of the measured and calculated values of the conductivities of the above mixtures, with the concentrations of the constituent solutions, and the data necessary for the calculations, viz , the dilutions of the respective electrolytes and their ionic concentrations, in the mixtures, these data being obtained by Prof. MacGregor's graphical process. The measured values of the conductivity were obtained from the above observations by graphical interpolation.

The results of Bender's experiments, as calculated by Prof. MacGregor (*Trans. N. S. Inst. Sci.*, ix., p. 101), are given below for comparison.

* *Transactions of the Nova Scotian Institute of Science*, vol. ix., Session 1895-96.

| Concentration (Grm.-mols. per litre). | | Conductivity. | | Difference, per cent. |
|---|---|---|---|---|
| KCl. | NaCl. | Measured. | Calc. | |
| 2·0 | 2·0 | 1445 | 1458 | +0·90 |
| 3·0 | 2·0 | 1823 | 1808·6 | −0·79 |
| 2·0 | 3·0 | 1664 | 1660 | −0·24 |
| 3·0 | 3·0 | 2007 | 1988·7 | −0·91 |
| 2·0 | 4·0 | 1858 | 1849·3 | −0·47 |
| 3·5 | 4·0 | 2303 | 2239·2 | −2·77 |
| 4·0 | 4·0 | 2432 | 2345·3 | −3·56 |

The two sets of observations agree very well together, the differences between calculated and observed values being of the same sign and in general for mixtures of about the same mean concentration of approximately the same magnitude.

The two series of mixtures of strong solutions show that the differences increase rapidly as the constituent solutions are more and more nearly saturated, reaching in the case of practically saturated solutions 6·4 per cent.

#### (B).—Sodium Chloride and Hydrochloric Acid.

The conductivities of the following series of mixtures of hydrochloric acid and sodium chloride solutions were measured :—

| Constituent solutions. Concentration (Grm.-mols. per litre). | | Conductivity of mixture, ×10⁸. |
|---|---|---|
| NaCl. | HCl. | |
| 2·02 | 4·55 | 4932 |
| ,, | 3·89 | 4492 |
| ,, | 3·29 | 4089 |
| ,, | 3·19 | 4073 |
| ,, | 3·06 | 3958 |
| ,, | 2·66 | 3623 |
| ,, | 2·56 | 3489 |
| ,, | 2·34 | 3323 |
| 1·04 | 4·55 | 5069 |
| ,, | 3·97 | 4682 |
| ,, | 3·80 | 4315 |
| ,, | 3·10 | 3989 |
| ,, | 2·86 | 3696 |
| ,, | 2·18 | 3112 |
| ,, | 2·11 | 3025 |
| ,, | 1·93 | 2824 |
| ,, | 1·58 | 2427 |
| ,, | 1·15 | 1928 |
| 0·607 | 1·120 | 1813 |
| ,, | 0·970 | 1620 |
| ,, | 0·815 | 1412 |
| ,, | 0·730 | 1296·5 |
| ,, | 0·603 | 1114 |
| ,, | 0·485 | 952 |

Table B contains in cols. 1 and 2 the concentrations of the solutions of hydrochloric acid and sodium chloride which were mixed, and in col. 7 the measured conductivities of the mixtures, obtained by graphical interpolation from the above observations. Cols. 3, 4, and 5 give the common concentration of ions and the respective dilutions of the electrolytes, in the mixture, as determined by Prof. MacGregor's graphical process. Col. 6 gives the calculated values of the conductivity, and the 8th the excesses of the calculated over the observed values expressed as percentages.

It will be seen that in the series of weakest solutions the differences between calculated and observed values are of such small magnitude and show such alternation of sign as to warrant the conclusion that they are due chiefly to accidental errors. In the two series of stronger solutions the differences are more irregular in magnitude and the alternation of sign is much less marked, the most of the differences being positive. The above results, therefore, seem to show that even in the case of two electro-

## Table A.

| Constituent solutions (Grm.-mols. per litre). | | Dilution in the mixture. | | Concentration of ions in the mixture. | Conductivity, ×10⁸. | | Difference, per cent. |
|---|---|---|---|---|---|---|---|
| KCl. | NaCl. | KCl. | NaCl. | | Calc. | Measured. | |
| 3.75 | 5.12 | 0.247 | 0.143 | 2.013 | 2312 | 2469 | −6.4 |
| 3.50 | ,, | 0.234 | 0.156 | 1.993 | 2276 | 2420 | −6 |
| 3.00 | ,, | 0.205 | 0.1855 | 1.950 | 2202 | 2313 | −4.8 |
| 2.50 | ,, | 0.175 | 0.216 | 1.890 | 2109 | 2190 | −3.7 |
| 2.00 | ,, | 0.151 | 0.239 | 1.822 | 2013 | 2049 | −1.7 |
| 3.88 | 5.00 | 0.26 | 0.14 | 2.014 | 2323 | 2481 | −6.4 |
| ,, | 4.50 | 0.291 | 0.151 | 1.998 | 2295 | 2429 | −5.5 |
| ,, | 4.00 | 0.335 | 0.166 | 1.980 | 2292 | 2377 | −3.6 |
| ,, | 3.50 | 0.388 | 0.182 | 1.955 | 2261 | 2324 | −2.7 |
| ,, | 3.00 | 0.462 | 0.205 | 1.916 | 2227 | 2260 | −1.4 |
| ,, | 2.50 | 0.573 | 0.227 | 1.864 | 2174 | 2189 | −0.7 |
| ,, | 2.00 | 0.750 | 0.250 | 1.788 | 2096 | 2116 | −1.0 |
| 3.46 | 3.12 | 0.412 | 0.2295 | 1.848 | 2130.5 | 2160 | −1.3 |
| 2.23 | 3.80 | 0.2432 | 0.2824 | 1.68 | 1875.5 | 1877 | −0.08 |
| 2.87 | 4.69 | 0.225 | 0.202 | 1.924 | 2177 | 2222 | −2 |

## Table B.

| Constituent solutions. Concentration (Grm.-mols. per litre). | | Concentration of ions in the mixture. | Dilution in the mixture. | | Conductivity of mixture, ×10⁸. | | Differences, per cent. |
|---|---|---|---|---|---|---|---|
| HCl. | NaCl. | | HCl. | NaCl. | Calc. | Measured. | |
| 2 | 2.02 | 1.272 | 0.539 | 0.451 | 3020 | 3008 | +0.4 |
| 2.5 | ,, | 1.392 | 0.592 | 0.398 | 3489.5 | 3456 | +1.0 |
| 3.0 | ,, | 1.485 | 0.636 | 0.354 | 3885 | 3888 | −0.08 |
| 3.5 | ,, | 1.570 | 0.668 | 0.322 | 4233.5 | 4260 | −0.6 |
| 4.0 | ,, | 1.665 | 0.700 | 0.290 | 4622.3 | 4580 | +1.0 |
| 4.5 | ,, | 1.740 | 0.726 | 0.264 | 4944 | 4880 | +1.3 |
| 1 | 1.04 | 0.744 | 1.031 | 0.892 | 1751 | 1752 | −0.005 |
| 1.5 | ,, | 0.916 | 1.215 | 0.708 | 2373 | 2332 | +1.7 |
| 2.0 | ,, | 1.062 | 1.345 | 0.578 | 2928.3 | 2900 | +0.9 |
| 2.5 | ,, | 1.196 | 1.431 | 0.492 | 3428.5 | 3398 | +0.9 |
| 3.0 | ,, | 1.324 | 1.495 | 0.428 | 3906 | 3872 | +0.9 |
| 3.5 | ,, | 1.440 | 1.555 | 0.378 | 4340.7 | 4316 | +0.6 |
| 4.0 | ,, | 1.538 | 1.585 | 0.338 | 4715 | 4700 | +0.3 |
| 4.5 | ,, | 1.628 | 1.616 | 0.307 | 5055 | 5036 | +0.4 |
| 0.4 | 0.607 | 0.392 | 1.450 | 1.844 | 829.8 | 838 | −1.0 |
| 0.5 | ,, | 0.436 | 1.636 | 1.656 | 983.4 | 976 | +0.8 |
| 0.6 | ,, | 0.474 | 1.794 | 1.500 | 1125.5 | 1116 | +0.8 |
| 0.7 | ,, | 0.508 | 1.922 | 1.372 | 1255 | 1250 | +0.4 |
| 0.8 | ,, | 0.544 | 2.022 | 1.272 | 1384.7 | 1388 | −0.2 |
| 0.9 | ,, | 0.582 | 2.121 | 1.173 | 1524.6 | 1525 | −0.025 |
| 1.0 | ,, | 0.620 | 2.195 | 1.099 | 1658.6 | 1656 | +0.16 |
| 1.1 | ,, | 0.655 | 2.267 | 1.027 | 1787.6 | 1784 | +0.2 |
| 1.2 | ,, | 0.692 | 2.322 | 0.972 | 1917.1 | 1913 | +0.2 |

lytes with a common ion, which differ so markedly in ionic velocity from one another as sodium chloride and hydrochloric acid, the dissociation theory enables us to calculate the conductivity of solutions containing both, within the limits of experimental error, up to a mean concentration of about 1 grm.-molecule per litre, and that in the case of solutions of greater mean concentration, the calculated value is greater than the observed.

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**Colorimetric Determination of Phosphoric Acid in Water.** — Alessandria (*Pharm. Central Halle*). — The author uses the molybdenic mixture; and as a liquid for comparison, he takes a solution of 0.1 grm. calcium phosphate in a few drops of nitric acid, diluting first to 1 litre and then further. Silica must be previously eliminated. A high percentage of phosphoric acid is not objectionable from a sanitary point of view if derived from fossils, bones, &c.

## HYDROFLUORIC ACID.*

By CARL F. STAHL.

(Concluded from p. 37).

### C.—Sulphuric Acid.

PLACE the platinum dish containing 4 grms. of the acid to be tested on a water-bath under a hood with a good draught and evaporate till acid fumes have completely ceased to be given off. Titrate the remaining syrupy liquid, which contains the free sulphuric acid, cold, with normal acid solution, using either litmus or phenolphthalein as indicator. The number of c.c. used we call "*c.*"

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The reactions involved are as follows:—

(2)　　　　　$HF + NaOH = NaF + H_2O.$
　　　　　　20　　　40　　　42　　　18

(3)　$SiF_4(HF)_2 + 6NaOH = 6NaF + SiO_2 + 4H_2O.$
　　　144　　　　240　　　252　　60　　72

(4)　$SiF_4(KF)_2 + 4NaOH = 4NaF + 2KF + SiO_2 + 2H_2O.$
　　220　　　160　　　168　　116　　60　　　36

(5)　　　$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$
　　　　98　　　80　　　142　　　36
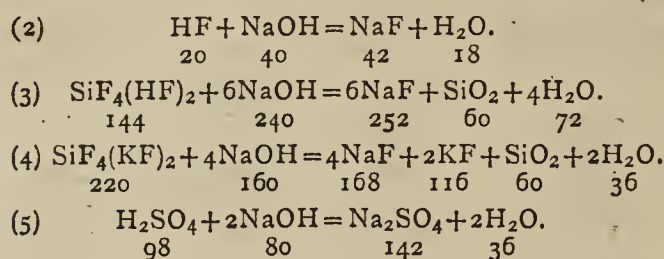
Now the number of c.c. of normal soda solution used in the first titration, and called "*a*," represents the alkali necessary to neutralise the hydrofluoric acid, hydrofluosilicic acid, and sulphuric acid, and in order to find the number of c.c. used for hydrofluoric acid alone, we have to subtract those used for hydrofluosilicic acid and sulphuric acid, but although we used the same weight (2 grms.) for the determination of the hydrofluosilicic acid, it would not be correct to subtract the number of c.c. used, because in the potassium silicofluoride two atoms of fluorine are neutralised, and we only neutralise with normal solution the remaining four atoms, which are combined with silicon. It would therefore have required—

$$b + \frac{b}{2} \; \text{c.c.}$$

to neutralise the free acid.

Having employed 4 grms. of substance for the determination of the sulphuric acid, the number of c.c. used for that determination must be divided by 2. The number of c.c. used for hydrofluoric acid alone are therefore equal to—

$$a - \left(\frac{3}{2}b + \frac{c}{2}\right),$$

and as each c.c. normal solution indicates 0·020 grm. HF, and 2 grms. of substance have been used, the number of c.c. found by the above formula express, without further calculation, the percentage of free hydrofluoric acid. Therefore—

$$a - \left(\frac{3}{2}b + \frac{c}{2}\right) = \text{per cent free hydrofluoric acid.}$$

After the foregoing explanation, the calculation of the percentage of hydrofluoric acid is an easy matter. 1 c.c. normal sodium hydroxide indicates 0·055 grm. potassium silicofluoride, which was obtained from 0·036 fluosilicic acid; having used two grms. of substance, 0·036 has to be divided by 2 and multiplied by 100 to get the percentage, or—

$$b \times 1\cdot8 = \text{per cent hydrofluosilicic acid.}$$

The percentage of free sulphuric acid is obtained by multiplying *c*, the number of c.c. used, by 0·048, dividing by 4, and multiplying by 100, or—

$$c \times 1\cdot2 = \text{per cent free sulphuric acid.}$$

Other free acids, muriatic or nitric acid, which influence the accuracy of the determination, are not likely to occur in commercial hydrofluoric acid, and their presence can easily be detected by well-known analytical methods.

To give an idea of the composition of some of the makes of hydrofluoric acid I have appended a few of the analyses made in the course of five years:—

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|---|---|---|---|---|---|---|---|---|
| Specific gravity .. | — | 1·299 | 1·264 | 1·253 | 1·244 | 1·264 | 1·282 | 1·247 | 1·234 |
| | P.c. | P.c. | P.c. | P.c. | P.c. | P.c. | P.c. | P.c. | P.c. |
| Hydrofluoric acid .. | 39·6 | 42·2 | 44·3 | 48·1 | 48·6 | 51·1 | 54·2 | 48·6 | 33·5 |
| Hydrofluosilicic acid | 2·7 | 14·9 | 10·1 | 4·7 | 5·0 | 6·8 | 8·1 | 6·3 | 10·6 |
| Free sulphuric acid . | — | 0·8 | 0·8 | 4·0 | 1·9 | 1·4 | 1·2 | 0·8 | 1·6 |

1. Oct., 1891. Baker and Adamson, C. P. acid in ceresine bottle, 0·005 per cent non-volatile residue.
2. Oct., 1891. Manufactured by J. C. Wiarda, sample received.
3. Nov., 1891. Manufactured by J. C. Wiarda, sample taken from package of 100 lbs.
4. Jan., 1892. Manufactured by James Irwin and Co., sample of lot of 3500 lbs.
5. Mar., 1892. Manufactured by James Irwin and Co., sample of lot of 3400 lbs.
6. Jan., 1894. Manufactured by Bender and Aldred, sample taken from package of 100 lbs.
7. Jan., 1895. Manufactured by James Irwin and Co., sample taken from tank holding 3000 lbs.
8. Oct., 1895. Manufactured by James Irwin and Co., sample taken from tank holding 3200 lbs., 0·015 per cent non-volatile residue.
9. Jan., 1896. So-called "pickling acid," sample received from a foundry.

By comparing analyses Nos. 2 and 7, it can be seen what influence hydrofluosilicic acid has in raising the specific gravity; although No. 2 has a higher specific gravity than No. 7, it contains 12 per cent less hydrofluoric acid, but $6\frac{8}{10}$ per cent more hydrofluosilicic acid. Nos. 3 and 6 have the same specific gravity, but No. 6 contains $6\frac{8}{10}$ per cent more hydrofluoric acid, and $3\frac{3}{10}$ per cent less hydrofluosilicic acid. The influence of sulphuric acid on the specific gravity can be seen by comparing Nos. 4 and 5.

A great difficulty in the manufacture of hydrofluoric acid is the very disagreeable and dangerous nature of the gaseous and liquid acid. The effects of the fumes on the respiratory organs are more injurious than those of other acids. Still more marked are the effects of the liquid acid on the skin. One drop of acid, although it does not make itself felt for a few hours, will, even on the horny skin of a workman's hand, cause a very painful inflammation in one-half day. Against the fumes the workmen protect themselves by respirators, or by the simpler way, which they usually prefer, of tying a handkerchief over nose and mouth and by greasing the unprotected parts of the face with lanolin. The latter is as effective as vaseline and easier to wash off. Against liquid acid rubber gloves afford protection. If liquid acid comes in contact with the skin it should be washed off at once with water and aqua ammonia, or another alkali, which will prevent injury.

In conclusion, I wish to say a few words about the different applications of commercial hydrofluoric acid.

The oldest, and up to the present time most extensive, application is for etching glass. For this purpose it can be applied in three different ways. In the gaseous form by suspending the articles to be etched over a mixture of fluor-spar and sulphuric acid. This is the oldest way of etching, and I believe most burettes, graduated cylinders, &c., for laboratory use are still marked in this way. If applied in gaseous form the acid leaves the surface opaque, while the liquid acid leaves the surface smooth and transparent. For the production of an opaque surface with liquid acid many empirical formulæ are published, and every glass factory, or rather every etching boss, has his own secret formula. But they all aim to produce a mixture of hydrofluoric acid with a fluoride of ammonium, or potassium, or sodium, with which a number of other substances, such as sulphuric, acetic, or muriatic acids, or ammonium or potassium sulphate, &c., are mixed, but it seems quite unnecessarily. Hydrofluoric acid prepared for etching opaque, goes under the trade name of "white acid." Lead glass is very rapidly and uniformly etched, and acid of 45 to 48 per cent is usually employed, while lime glass requires a stronger acid and more time. Lately, acid as strong as 52 per cent HF is employed. "White acid" is much more convenient for application than gaseous acid, and acts very rapidly; for instance, a lead glass lamp chimney can be rendered opaque by simply dipping it into the acid for one minute. Lime glass, even with acid specially prepared for it, requires about two minutes immersion. It is important that the temperature of the acid and the glass should be about 15°

C. Parts of the glass which are to remain unetched, must be protected. For this purpose a number of substances are in use. Asphaltum varnish is usually employed, when the design is printed on paper and then transferred to the glass; for the so-called needle-work, a mixture of Burgundy pitch and bees'-wax is used.

A more recent application of hydrofluoric acid is for cleaning castings from sand. These have so far been cleaned, either by mechanical means or with sulphuric acid; but the first is expensive, and neither way, in many cases, satisfactory. The sulphuric acid loosens the sand by dissolving the iron to which it is attached, while hydrofluoric acid dissolves the sand itself and therefore acts more promptly and does not cause any loss of iron. It also dissolves the magnetic oxide formed on the surface of the iron very readily, much more so than sulphuric acid. This latter point is important for castings which have to be worked afterwards with edged tools, the magnetic oxide being very hard. For cleaning castings, the acid is diluted to about 1 or 2 per cent HF; the pickling can therefore be carried on in wooden vessels.

Some of the firms who use hydrofluoric acid for cleaning iron have kindly sent me reports on it. The most interesting parts of these reports I will mention here with their permission :—

Mr. S. H. Stupakoff, Supt. Union Switch and Signal Co., writes :—

"We use the acid in the proportion of $2\frac{1}{2}$ quarts to one-half barrel water, containing about 25 gallons,"— equal to one pound 48 per cent hydrofluoric acid in 35 pounds of water, the liquid would therefore contain $1\frac{4}{10}$ per cent HF—"the bath is filled to the top with castings and they are left in it for about half an hour. We can renew our charge by adding each time one quart of acid.

"We find that the hydrofluoric acid is vastly superior to sulphuric acid, as the latter will not pickle satisfactorily in less than one day, and besides this we use about double the quantity of sulphuric acid compared with hydrofluoric acid to pickle the same amount of castings." (As the quantities given by Mr. Stupakoff are by volume, this would be equal to one pound of 93 per cent sulphuric acid in 11 pounds of water; the liquid would therefore contain $8\frac{1}{4}$ per cent sulphuric acid, or six times as much as the hydrofluoric acid bath).

"With the sulphuric acid we experienced a great deal of trouble by obtaining a white sediment on the castings, which was very difficult to remove, even when washed in hot water. This white coating would frequently work through the paint with which the castings were subsequently covered.¶

"We had no occasion to try this acid for cleaning any other material but cast-iron, with the exception of one instance, when we tried to remove heavy coatings of rust from a lot of mixed material, consisting of cast-iron and wrought iron. The hydrofluoric acid did this to perfection, and left a perfectly bright surface.

"I can say, in conclusion, that I am perfectly satisfied that the use of hydrofluoric acid for the cleaning of new castings and corroded iron is certainly a success, and I will always prefer it to the old method of pickling in sulphuric acid."

From the engineer of another firm I received the following report :—

"The best solution is 1 to 30." (This is by volume, and the bath would contain, as he used 48 per cent hydrofluoric acid, about 2 per cent HF). "As we make no small castings of grey iron, I have only used the acid on malleable castings, with the result that small castings are cleaned excellently in two hours. I have also cleaned castings in a mixture of 1 acid to 50 water"—the bath would contain about 1 per cent HF—"by leaving them in over night, but we prefer to clean with the stronger acid. The pickling vat is usually filled up with castings three times before it requires more acid.

"It takes sulphuric acid twice as long with the same proportion"—that is, 1 to 30 would give a solution of about $5\frac{6}{10}$ per cent sulphuric acid—"and then does not eat into the corners as well as hydrofluoric acid; also wastes more iron, and does not leave it bright."

For iron which is to be enamelled, the cleaning with hydrofluoric acid is also advantageous, because it leaves a purer metallic surface than can be obtained with other acids.

I am informed that a large firm in this city is at present making arrangements with a view of throwing out their whole mechanical cleaning plant, in which they have been cleaning 60 tons a day.

Hydrofluoric acid or its salts is also used in distilleries to insure a more complete fermentation (Dr. Leo Backeland, *Journ. Am. Chem. Soc.*, xiv., 212).

The latest application, of which I heard only a few days ago, is for cleaning out oil and gas wells. It seems that the shooting of a well sometimes packs the rock so tightly that the hole is drier after the shooting than before. By pouring about six barrels of hydrofluoric acid (I suppose the acid is used diluted) into the hole, which dissolves the silicates and afterwards is pumped out again, gas or oil get an outlet.

# NOTICES OF BOOKS.

*Painters' Colours, Oils, and Varnishes*: a Practical Manual. By GEORGE H. HURST, F.C.S., Member of the Society of Chemical Industry; Lecturer on the Technology of Painters' Colours, Oils, and Varnishes at the Municipal Technical School, Manchester. Second Edition, Revised and Enlarged. With numerous Illustrations. London: Charles Griffin and Co., Ltd. (All rights reserved). Pp. 499.

MR. HURST has now fairly acquired recognition as an authority on the important class of compounds described in this work. He seems to use "assay" as synonymous with qualitative examinations, and in contradistinction to "analysis."

Among the white pigments we find China clay, the principal use of which is not as a pigment, but as a means of giving a specious body to calico. If introduced in aniline lakes for paper-staining and tissue-printing, its freedom from grit is a vital point.

Many substances are here described as substitutes for white lead, but, in spite of persevering efforts, that prospect of the displacement of that unsanitary body does not seem very near at hand. The "white leads" of Wilkinson and Pattinson have gone out of use.

Among red pigments a brief notice is given to mercuric iodide, $HgI_2$. This compound is often known as "brilliant scarlet" and as "geranium red." It is more permanent when obtained by grinding mercury and iodine together in proper proportions than when prepared by precipitation.

Pink colour, or stannic chromate, is not mentioned at all, though, according to the observations of Gentele and our own, it perfectly resists all external agencies.

In speaking of the chromes Mr. Hurst mentions the vicious custom of the trade calling pigments contaminated with lead sulphate "pure chrome," whilst common chromes contain barium sulphate, or any other cheap white base, in addition.

Chrome-red is remarkably rich in synonyms. Among these we find "Persian red,"—an *alias* of pink colour.

Among the ochres and sienna the Oxfordshire ochre is recognised as excelling all other ochres, both in brightness and covering power. The American ochres are described as being, for the most part, ochres in name only; one sample analysed by the author was found to contain 75 per cent of barium sulphate.

The "Mars colours" of the late George Field are described as having no advantage over ochres and iron

reds as regards brightness and permanence of tone, but as being more expensive.

Turner's yellow and Naples yellow have been greatly, if not entirely, superseded by the chromes. Turner's yellow was at one time known as Montpelier yellow, Kassel yellow, Verona yellow, and mineral yellow.

King's yellow, an arsenical colour, $As_2S_3$, is fortunately in much less repute than it was formerly.

The Brunswick greens now made are, in fact, mixtures of Prussian blue and of chrome-yellow, whilst the old Brunswick green is — or rather was — a basic copper chloride. It was too expensive, owing to the tediousness of its preparation.

True chrome-greens, such as that of Guignet, are strongly recommended, and are carefully distinguished from the mixtures of Prussian blue and chrome-yellow often sold under the same name. The insolubility of Guignet's green renders it perfectly unobjectionable from a sanitary point of view.

Emerald-green is a beautiful colour, but as an arsenical compound it affects the health of persons making it or using it, in a most capricious manner, depending on physiological idiosyncracy. If exposed to damp air it undergoes gradual decomposition.

Cobalt green (Rinman's green) is in little demand on account of its high price. The author points out that, should a cheap source of cobalt be discovered, it might come into extensive use.

Cœruleum, the old Egyptian blue colour, is at present an unsolved riddle as to the method of its preparation, unless the recent announcement by a French chemist should be verified.

Carmine is mentioned as the best type of a lake colour. Its composition is not by any means thoroughly known. The receipt of Madame Cenette, of Amsterdam, is defective. The author, like ourselves, has not succeeded in preparing a satisfactory carmine according to its direction.

Under the head of "Varnish-making" we learn that amber is found in the Hukong Valley, in North Burmah, at an elevation of 1050 feet above the sea-level, and is regularly mined for. The account given of the gums, or rather resins, used in varnish making, is very elaborate.

We do not think that there can be found in our scientific and technical literature any work which can compete with that of Mr. Hurst.

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*Ammonia : the New Procedures for its Manufacture and its Applications.* ("L'Ammoniaque : ses Nouveaux Procédés de Fabrication et ses Applications"). By P. TRUCHOT. Paris : Bernard Tignol.

THIS valuable monograph forms No. 64 of the "Bibliotheque des Actualites Industrielles," and is a work of most unquestionable merit. The demands for ammonia have multiplied and extended to such an extent that the search for new and improved sources of this necessary compound has been intensified throughout the civilised world. No longer can we content ourselves with the destructive distillation of animal matter, such as camel's dung or horns and bones. Every chemical process in which nitrogen is thrown off in combination with hydrogen is made to contribute its quota. Yet so great is our need for ammonia, that further supplies are still called for. Almost incalculable wealth is awaiting the inventor who can prevail upon the free nitrogen of the atmosphere to combine with hydrogen on a large scale, but hitherto "the haughty demon mocks our spell."

M. Truchot commences his task with physical considerations bearing upon the manufacture of ammonia, such as the specific gravities of ammonia and its salts, their melting- and boiling-points, indices of refraction, specific heats, solubilities in water and alcohol, vapour-tensions, densities, and boiling-points of saturated solutions, thermo-chemical data, refrigerating mixtures, and a comparison of the various hydrometric standards. It is scarcely needful to say that the author clings to Baumé despite its inconveniences.

The second chapter gives us the history of ammonia from Pliny, Dioscorides, and Ramon Lulli.

In the third chapter follow the chemical and physical properties of ammonia and of the ammonium salts, their behaviour with heat, with electricity, with oxygen and platinum sponge, with the halogens, sulphur and boron; and the modes of formation of ammonia.

In the fourth chapter we pass to the manufacture of ammonia from natural products, from atmospheric nitrogen, from coal, from nitrate of soda, from nitrogenous organic matters, from urine, sewage, excrements, vegetable dregs, and peat.

Coal is rightly described as constituting at present the main source of ammonia, whether as a by-product of the gas manufacture, or in coke burning, or in the working of blast-furnaces.

It is estimated that if all coke-ovens were fitted for the condensation of the by-products, we should have from this source a yearly yield of 273,000 tons sulphate of ammonia, the chief part of which is still going to waste. The number of coke ovens properly fitted for this purpose in Britain is only 413, whilst in Germany more than 1250 are in action; though we manufacture about double the quantity of coke.

Mr. Mond, calculating the amount of fuel burnt yearly in Britain at 150,000,000 tons, estimates that if only one-tenth of this quantity were treated by his process our annual production of sulphate of ammonia would reach the enormous figure of five million tons!

The synthetic production of ammonia is most carefully and thoroughly considered. Nitrogen and hydrogen have been made to combine by various experimentalists, but the processes unfortunately are not remunerative.

In spite of numerous assertions and varied researches, the reactions attempted have never proved practical, or at least not capable of industrial success. The intervention of boron and titanium has not been remunerative.

It is, of course, demonstrated that certain vegetables, by virtue of lower plants which are attached like tubercles to their roots, are able to supply themselves with synthetic ammonia, and can thus dispense with nitrogenous manures. For the details of this most important subject the reader is referred to the lectures of Georges Ville, translated by W. Crookes, F.R.S. (Longmans).

M. Truchot's work includes instructions for the analysis of ammonia and its salts, of nitrogenous substances, and and of ammonia in waters and in crude coal-gas.

The applications of ammonia and of the ammoniacal salts are treated at some length, and there is a summary of the principal patents concerning the compounds, and a brief bibliography.

The work deserves very emphatic recommendation.

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**Influence of Trees on Malaria.**—A medical contemporary mentions, on the authority of Dr. Alexander, Medical Officer of Health for Poplar and Bromley, that the planting of osiers on a large scale in North-western India has been useful in stamping out malaria in a notoriously unhealthy valley covered with stagnant pools. Sanitarians will do well to bear this fact in mind.

**Detection of Dulcin in Beverages.** — Morpurge (*Pharm. Central Halle*) evaporates the liquids with 1-20th part of lead carbonate, and extracts repeatedly with alcohol. From the dry residue of the united alcoholic extracts approximately pure dulcin can be extracted with ether. The liquid is heated for a short time with 2 drops of phenol and 2 drops of concentrated sulphuric acid; the syrup thus formed is diluted with a few c.c. of water, and the solution is superstratified in a test-tube with a little ammonia. If dulcin is present, the surface of contact of the two liquids takes a blue or violet colour.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxii., No. 26, June 29, 1896.

M. Albert Gaudry announced to the Academy the death of Sir Joseph Prestwich, a correspondent of the Academy in the Geological Section.

The Academy proceeded to nominate a correspondent for the section of Astronomy, *vice* Prof. Newcomb, who has been elected a Foreign Associate. M. Backhuyzen was elected by a large majority.

**Spectrum of Phosphorus in Fused Salts, and in certain Metallurgical Products.**—A. de Gramont.—(See p. 41).

**On Blue Nitrosodisulphonic Acid, and on some of its Salts.**—Paul Sabatier.—This acid has the composition $NO(SO_3H)_2$. The sulphuric solutions of the free acid are gradually decomposed at ordinary temperatures into sulphuric acid, sulphurous anhydride, and nitric oxide. This decomposition is not very rapid at 100°. If agitated with air, the solutions are quickly decomposed by oxidation, giving off nitrous vapours and forming nitrosulphuric acid. A solution of hydrogen peroxide in concentrated sulphuric acid effects a rapid decolouration. Chlorine produces an analogous result, but bromine acts much less rapidly, and remains for some time as a greenish solution. Iodine used in a sulphuric acid solution has scarcely any action. Water destroys the compound, with the production of nitrous gas and sulphuric acid. The addition to the blue liquid of most metallic oxides, anhydrous or hydrated, and also of carbonates, generally brings on a violent action, which leads to the destruction of the blue acid and the exclusive production of sulphates. This takes place with the alkaline and alkaline-earthy oxides or carbonates; those of nickel, cobalt, magnesium, aluminium, silver, lead, cadmium, and zinc. Ferric acid introduced into the refrigerated blue liquid at about 0° gradually dissolves without any escape of gas, yielding a vinous-rose liquid. Green cupric carbonate gives a deep blue solution, with an escape of carbonic gas; the solution is rather more violet than the acid which has produced it, and of an incomparably more intense shade. A bright iron nail plunged into the nitrososulphuric solution is immediately covered with a very brilliant rose tint, and there soon appear rose-coloured threads setting out from the metal and diffusing themselves in the liquor, which they colour of a rose-cobalt shade, more and more intense. This is a fine lecture experiment.

**Action of Iodine upon Stannous Chloride.**—V. Thomas.—The author expected that stannous chloride must be capable of fixing iodine so as to give rise to an addition chloro-iodide, $SnCl_2I_2$. Anhydrous stannous chloride, finely powdered, was placed in a perfectly dry flask; upon the stannous chloride there was introduced carbon disulphide holding iodine in solution. This was at first rapidly decolourised, then by degrees the violet-red tint of the iodine gave place to a pale yellow tint, which grew gradually deeper, and soon became a reddish orange. It results from the author's experiments that tin chloro-iodide cannot be obtained in this manner.

**New Method for the Preparation of Aromatic Aldehyds.**—L. Bouveault.—In former papers the author has given an account of the attempts which he has already made to convert the glyoxylic acids of the aromatic series into aldehyds. He has now found that this transformation can be effected in a quantitative manner by means of aniline.

**Thermic Researches on Uranium Compounds.**—J. Aloy.—The author has studied the solution-heats of the principal soluble salts of uranyl, and the formation-heats of the dissolved salts of uranyl.

**Researches on the Chloridation of Gallic Acid. Formation of Dichlorogallic Acid and of Trichloropyrogallol.**—Alexander Biétrix.—The products of the chloro-substitution of gallic acid have not yet been prepared. On passing a current of chlorine into an aqueous solution of gallic acid, we remark the appearance of a black colour, which disappears on the prolonged action of the chlorine. The author examines the stages of this transformation.

**Crystallographic Properties of Benzylidene, Methyl- and Ethylsalicidenes, and Anisol Camphors.**—J. Minguin.—This memoir is not well suited for abstraction.

**Isanic Acid: a New Non-saturated Fatty Acid.**—Alex. Hébert.—The I'sano seeds from the Loango country, known also as Ungueko, are derived from a large tree of the family of Olacineæ. In the oil the author has recognised three fatty acids:—1. A liquid yellow acid, which we have named oleic acid, and which forms about 15 per cent of the total acids. 2. A liquid acid, brown and highly oxidisable; its properties are those of linoleic acid, and its proportion is about 75 per cent. 3. A white solid acid, present in the proportion of about 10 per cent. This acid is present in fine leafy crystals, fusible at 41°, very soluble in strong alcohol, ether, chloroform, benzene, acetone, methylic alcohol, and petroleum ether. Its composition is $C_{14}H_{20}O_2$.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 1.

**Detection of Saccharin in presence of Salicylic Acid.**—Hr. Hairs (*Pharm. Central Halle*).—The author eliminates the salicylic acid as bromosalicylic acid. The liquid is then acidulated with hydrochloric acid and mixed with a moderate excess of bromine water. The bromosalicylic acid is filtered off, freed from excess of bromine by a current of air, and extracted with ether.

**Determination of Halogens in Organic Substances.**—J. Walker and J. Henderson (CHEM. NEWS).

**Determination of Alkyl combined with Nitrogen.**—J. Herzig and H. Meyer (*Monatshefte fur Chemie*).

**Determination of Formic Acid.**—A. Lieben titrates with permanganate in a solution rendered alkaline with soda. (See *American Chemical Journal*, xvii., No. 7.)

**Determination of Milk-Sugar.**—G. Denigès (*Journ. de Pharm.*).—The colour of cow's milk is yellowish, and of goat's milk pure white.

**Zinc in American Apple-Rings.**—R. Hefelmann (*Pharm. Central Halle*).—Is probably due to the international addition of zinc-salts. (To what end?)

**Preservation of "Hack-flesh"** (*Forsch. Berichte über Lebensmittel*).—H. Kämmerer.—For the preservation of this disgusting substance, sodium sulphite or the corresponding bisulphite is added.

**Examination of Caviare.**—Niebel (*Zeit. fur Fleisch und Milk Hygiene*). — According to the author, caviare should be neutral to litmus and contain neither free ammonia nor hydrogen sulphide.

**Detection of Mineral Acids in Presence of Organic Acids, especially in Vinegar.**—Niokel (*Pharm. Zeitung*) uses the well-known violet colour of lignin by mineral acids with phloroglucine. The vinegar is mixed with phloroglucine, and a splinter of pine-wood or a fragment of bamboo is boiled in the liquid for some time.

**Microchemical Determination of Starch and Ethereal Oils in Adulterated Cloves.** — H. Krämer (*American Pharm. Association*).

**Determination of Sugar.**—R. Farnsteiner (*Forschungs Berichte über Lebensmittel*, ii., 235).

**Volumetric Determination of Sugar.**—Zdenek Peska.—The author recommends the modification of Fehling's solution, proposed by Pavy. (See CHEMICAL NEWS, lxxi., p. 235).

**Determination of Thiophen in Benzene.**—(From *Comptes Rendus*, cxx., p. 781).

**Determination of Anthracen.** — H. Bassett (CHEM. NEWS, lxxi., p. 202).

**The Chemical Laboratory of the Brewer.** — W. Windisch. — A highly commendatory notice of a special work.

**Analysis of Fats, Oils, and Waxes.**—Hr. Benedikt.—English version by J. Lewkovitsch (Macmillan).

**Examination of Water.** — H. Nordlinger (*Pharm. Central Halle*).—In order to detect the possible entrance of cesspool liquids into wells, the author makes use of saprol. Cresoliferous disinfectants can be detected by smell at the dilution of $1:1,000,000$, and by the characteristic taste if diluted to $1:2,000,000$.

**Distinction between Ground Rice and Buckwheat.**—A Lehn and Hansek.— The latter authority finds a microscopic comparison sufficient.

**Determination of Fats in Foods without previous Desiccation.**—Hr. Hefelmann (*Pharm. Central Halle*) uses Werner Schmid's method for the determination of milk fat (*Zeit. Analyt. Chemie*, xxvii., p. 464).

**Ash in Commercial Milk - sugar.** — Braithwaite (*Pharm. Central Halle*).—In pure sorts the ash should not exceed 0·25 per cent.

**Examination of Milk.**—Notices of the determination of the specific gravity of coagulated milk by Mats Weibull (*Pharm. Central Halle*); determination of solids and fats in milk, by H. Weller (*Forschungs-berichte über Lebensmittel*); determination of albumenoids in milk, Gruber (*Zeit. f. Nahrungsmittel Untersuch.*) multiplies the total nitrogen by 6·37, instead of 6·5. Against this proposal Meissl objects.

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## NOTES AND QUERIES.

*⁎⁎* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Elecrolytic Separation of Copper.**—Can you give in your much esteemed paper a method for the electrolysis of copper bullion containing arsenic, antimony, gold, and silver; that is, how to keep the four metals mentioned in solution while the copper precipitates. Also, can you give a method for the determination of As and Sb in copper bullion, where these metals are present in quantities less than one-tenth of 1 per cent.—C. S. RICHARDSON.

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# THE CHEMICAL NEWS.

## COAL - DUST.

### THE QUESTION OF PRIORITY.

### By W. GALLOWAY.

IN the report of a lecture given *in extenso* at page 64, *et seq.*, in the *Colliery Guardian*, of the 10th inst., on "Coal-dust and Explosives, by Mr. H. Richardson Hewitt, of Derby, H.M. Inspector of Mines, the following remarkable statements occur :—

> " It was but a few years ago that the Messrs. Atkinson
> first drew attention to their idea that coal-dust
> was a dangerous element in mines where blasting
> operations were carried on. . . . . "

> "After Messrs. Atkinson first drew attention to the sub-
> ject Professor Galloway took it up and made some
> rough experiments by placing gunpowder cartridges
> in heaps of coal-dust and firing them in the dark."

Although these statements were obviously uttered in ignorance of the nature of my experiments, they raise a distinct and palpable issue as to priority.

The facts are as follow :—

My first experiments with coal-dust were made on the 3rd of July, 1875. I then discovered that a mixture of air and fire-damp which is not inflammable at ordinary pressure and temperature, on account of the smallness of the proportion of fire-damp present in it, becomes inflammable when coal-dust is added to it, and can be ignited by means of a comparatively small flame.

On the 22nd of December, 1875, I gave evidence in the capacity of Assistant Inspector of Mines at the Coroner's inquest on the Llan Colliery explosion (South Wales District), when I attributed that explosion principally to the influence of coal-dust. My evidence was dis-countenanced by the Chief Inspector of Mines for the district, and was not embodied in the Reports of the Inspectors of Mines, but it was reported *verbatim* in the two local newspapers (*Western Mail* and *South Wales Daily News*) of 23rd December, 1875.

On the 2nd of March, 1876, I read my first paper, entitled " On the Influence of Coal-dust in Colliery Explosions," before the Royal Society. In that paper I announced the coal-dust theory.

In 1878 I published a large number of articles in *Iron* under the title of " Coal-dust Explosions." In these articles, amongst many other things, I quoted and commented upon what Faraday and Lyell had written about coal-dust upwards of twenty years previously, and I gave complete translations of the papers that had been published in France having a bearing upon the subject.

Besides contributing a number of other articles and papers on the same subject to various societies and periodicals, I read altogether five papers " On the Influence of Coal-dust in Colliery Explosions " before the Royal Society, viz., 2nd March, 1876, already referred to ; 27th February, 1879 ; 30th May, 1881 ; 29th December, 1881 ; 8th May, 1884 ; and one on " A Coal-dust Explosion," 17th February, 1887.

During the ten years ending in 1885 I was engaged from time to time in carrying out experiments with coal-dust ; first, with apparatus provided by the Glamorgan Coal Company, Limited, and erected at their Llwynypia Colliery ; secondly, with apparatus purchased by means of Government grants obtained through the Royal Society ; and, thirdly, with apparatus belonging to the Royal Commission on Accidents in Mines.

Before the accounts of my earlier investigations, and the conclusions founded upon them had appeared, the Inspectors of Mines and other mining experts were practically unanimous in attributing the cause of every great colliery explosion to the sudden outburst of a large volume of fire-damp which was supposed to have flooded the workings, become mixed with the air, and on being ignited in one way or another, produced the various phenomena subsequently observed. This explanation was accepted everywhere as the only one possible ; it was recorded in the official reports of the Inspectors of Mines, and they, as well as the experts of that generation, were irretrievably committed to it.

There was not, figuratively speaking, a ripple of dissent from this mode of explanation upon the placid surface of mining opinion at the moment the coal-dust theory was launched upon it.

At first the new theory was ignored ; then it was scouted ; then it was subjected to scathing criticism ; then it was taken up in a tentative manner by some of the younger and bolder men ; and, lastly, when it was found to be making serious headway, one of the more adventurous spirits suddenly discovered that it was not new after all, for had not Faraday and Lyell and certain French engineers been its real authors ?

Following my lead, first a joint paper by Messrs. Hall and Clarke was contributed to the North of England Institute, in May, 1876, then another by Messrs. Marrecco and Morrison, in 1878, all of whom, with the exception of Mr. Clark, had previously corresponded with me on the subject of explosions ; finally, in the year 1879, after the publication of my articles on " Coal-dust Explosions " in *Iron*, and during the next few years afterwards, a very great army of investigators, headed by Government Commissions in England, France, Prussia, and Saxony, and including the Messrs. Atkinson, entered the field.

Some of these investigators contented themselves with criticism pure and simple ; others, of whom many had neither aptitude nor training for the work, made experiments with small and imperfect apparatus, and, as a consequence, obtained only negative results ; still others were carried away by the side issues ; and only a few, such as the Prussian and Austrian Commissions, and Messrs. Hall and Atkinson, H.M. Inspectors of Mines, did really good and substantial work of an enduring kind.

The facts and conclusions recorded in my earlier papers were freely drawn upon ; by some they were generously acknowledged ; by others they were first denounced and then assimilated ; by others they were adopted without acknowledgment ; while some of my experiments, and notably my investigation into the nature of the fire-damp cap (*Proc. Roy. Soc.*, 2nd March, 1876), were repeated with some variations and described as if they were original.

A flood of literature was now poured upon the mining world from every side, embodying opinions of the most conflicting and mystifying character, such as a mixture of coal-dust and air may take fire but it cannot explode ; coal-dust can only carry flame from one accumulation of fire-damp to another ; a coal-dust flame cannot extend throughout the workings of a mine in the entire absence of fire-damp ; a small proportion of fire-damp must always be present in the air when an explosion takes place ; some kinds of coal-dust are more inflammable than others ; and so on—so that amid the din and hurly-burly of the strife the main question of how to put an end to great explosions was almost lost sight of.

But the scene of each successive explosion when viewed under the new light served gradually to dispel the Will-o'-the-Wisps which the majority of the investigators had been following pertinaciously for years ; and thus it has come to pass that the new generation of Inspectors of Mines, and those who have been associated with them in investigating the phenomena of explosions, have become convinced, I believe almost to a man, of the soundness of the coal-dust theory ; and that the struggle of contending

factions, which was at its height ten or twelve years ago, has gradually subsided, leaving us face to face with a work which still remains to be done, namely, to render the occurrence of a great colliery explosion impossible in the future.

Into the consideration of that problem I do not propose to enter on the present occasion, as I have lately done so in considerable detail in the pages of the *Daily Chronicle* of 24th June of the present year.

Cardiff, 17th July, 1896.

## A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF THE SOLUBLE COMPOUNDS OF IODINE.

### By Professor Dr. E. RIEGLER.

THE principle of the method is liberation of iodine in the iodides by iodic acid ($HIO_3$), solution in petroleum ether, determination of the excess of iodic acid by titration with a decinormal solution of sodium thiosulphate, and, from the quantity of iodic acid consumed, calculating the quantity of iodine corresponding to the iodide.

If a solution of iodic acid is brought in contact with the solution of an iodide, iodine is separated according to the following equation:—

$$6HIO_3 + 5NaI = 5NaIO_3 + 3H_2O + 6I;$$
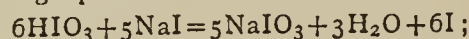
that is, to each atom of iodine liberated there belong $\frac{5}{6}$th atom of the iodide.

Now, as according to the above equation an atom of iodine corresponds to a mol. of iodic acid, it is evident that, instead of the iodine, we may determine the quantity of iodic acid consumed for liberating the iodine from the iodide.

The solution of iodic acid which I employ for this purpose is decinormal, and it is prepared by dissolving 17·6 grms. iodic acid ($HIO_3$) in 1 litre of distilled water. In preparing the decinormal solution of thiosulphate, we proceed from the decinormal solution of iodic acid.

If a solution of thiosulphate mixed with a solution of starch is brought in contact with a solution of iodic acid, there ensues the following transposition:—

$$6Na_2S_2O_3 + 6HIO_3 = Na_2S_4O_6 + 5NaIO_3 + NaI + 3H_2O.$$
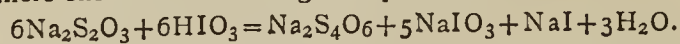
Consequently, as long as an excess of thiosulphate is present in the liquid, the starch is not coloured blue by the gradual addition of the solution of iodic acid; but in the moment when the first drop of this acid is added in excess, the iodine is liberated and colours the starch blue, which consequently acts as an indicator.

As it follows from the above equation, a mol. of sodium thiosulphate corresponds to each mol. of iodic acid, therefore 1-10th mol. of sodium thiosulphate corresponds to 1 litre decinormal solution of iodic acid,—*i.e.*, 17·6 grms. iodic acid correspond to 24·8 grms. crystallised sodium thiosulphate.

We weigh therefore about 28 grms. crystalline thiosulphate, dissolve it in a litre of water, test the solution with the decinormal solution of iodic acid, and dilute accordingly.

By means of these two decinormal solutions we determine in the following manner the iodine in the iodides under examination:—

Into a parting funnel with a ground glass stopper we introduce a known number of c.c. of the iodide solution (which must not be more concentrated than 1 per cent), add from a burette an equal number of c.c. of the decinormal solution of iodic acid, shake well up, add 20 c.c. of petroleum ether, into which the greater part of the liberated iodine passes after vigorous agitation; after about a quarter of an hour the liquid below the stratum of petroleum ether is allowed to run into a beaker by opening the glass cock. The solution of petroleum ether

is poured away out of the parting funnel, into which the liquid from the beaker is again introduced with about 15 c.c. of pure petroleum ether, which after vigorous shaking will take up the last residues from the liquid. The aqueous solution is now passed from the parting funnel into a small flask by opening the glass cock, and, after the addition of a little starch solution, the excess of iodic acid is titrated back by means of the decinormal thiosulphate solution. The number of c.c. of decinormal thiosulphate solution which show the excess of iodic acid are deducted from that of the decinormal iodic acid solution employed. The difference thus obtained, multiplied by the factor $0·0127 \times \frac{5}{6} = 0·0106$, gives as product the quantity of iodine corresponding to the decomposed iodide.

If the quantity of iodine found in this manner is multiplied by the factor 1·368, we find it expressed as potassium iodide; if multiplied by 1·1811, we obtain it as sodium iodide.—*Zeit. Analyt. Chemie*, xxxv., p. 305.

## THE COPPER ASSAY BY THE IODIDE METHOD.

### By ALBERT H. LOW.

THE last edition of Dr. Peters's "Modern Copper Smelting" contains a description of the writer's modification of the copper assay by the iodide method. The following description of the same method embodies whatever changes have been deemed desirable up to date, as the result of almost daily work upon copper ores and products. For the most accurate technical work I prefer it to all other methods. For practical work it exceeds the electrolytic method in accuracy, notwithstanding that the latter, when every precaution is taken, is perhaps theoretically more accurate.

*Copper Assay by the Iodide Method.*

Prepare a solution of sodium hyposulphite containing about 19 grms. of the pure crystals to the litre. Standardise as follows:—Weigh accurately about 0·200 grm. of pure copper foil, and place in a flask of about 250 c.c. capacity. Add 5 c.c. of a mixture of equal volumes of strong nitric acid (1·42 sp. gr.) and water, and thoroughly boil off the red fumes—a very essential point. Now remove from the lamp and add 6 to 7 grms. of crystallised zinc acetate, roughly weighed, and about 15 c.c. of water. Instead of adding the zinc acetate in this way, a cold saturated solution many be kept on hand and about 20 c.c. taken, the additional 15 c.c. of water being then unnecessary. Heat to boiling for a moment and then cool to ordinary temperature, and dilute to a bulk of about 50 c.c. Now add about 3 grms. of potassium iodide and shake it about gently until dissolved. Cuprous iodide will be precipitated, and iodine liberated according to the following reaction:—

$$2(Cu.2C_2H_3O_2) + 4KI = Cu_2I_2 + 4(K.C_2H_3O_2) + 2I.$$
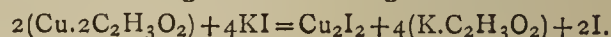
The free iodine colours the mixture brown. Titrate at once with the hyposulphite solution until the brown tinge has become weak, and then add sufficient starch liquor to produce a marked blue colouration. Now continue the titration cautiously until the blue tinge has entirely vanished. When almost at the end allow a little time after the addition of each drop to avoid passing the point. One c.c. of the hyposulphite solution will be found to correspond to about 0·005 grm. of copper. In the assaying of ores, &c., when half a grm. is taken, 1 c.c. of the standard hyposulphite would then equal about 1 per cent copper. The reaction between the hyposulphite and the iodine is—

$$2(Na_2S_2O_3) + 2I = 2NaI + Na_2S_4O_6.$$

Sodium iodide and tetrathionate are formed. The starch liquor may be made by boiling about half a grm. of starch

with a little water, and diluting with hot water to about 250 c.c. It should be used cold, and must be prepared frequently for regular work, as it does not keep very well. The hyposulphite solution made of the pure crystals and distilled water appears to be very stable, showing no appreciable variation at the end of a month, when kept under reasonable conditions.

### Treatment of Ores.

Treat half a grm. of the ore in a flask of 250 c.c. capacity with 5 or 6 c.c. of strong nitric acid, and boil gently nearly to dryness. Then add 5 c.c. of strong hydrochloric acid, and again boil. As soon as the incrusted matter has dissolved, add 5 c.c. of strong sulphuric acid and heat strongly, best by manipulating the flask in a holder over a small naked flame, until the more volatile acids are expelled and the fumes of the sulphuric acid are coming off freely. Allow to cool, and then add 20 c.c. of cold water, and heat the mixture to boiling, to thoroughly dissolve any anhydrous sulphates of iron, &c. Now filter to remove more especially any lead sulphate, and receive the filtrate in a beaker about 2½ inches in diameter. Wash the flask and filter with hot water, and endeavour to keep the volume of the filtrate down to about 50 or 60 c.c. Place in the beaker two pieces of sheet aluminum, which, for the sake of convenience in subsequent washing, may be prepared as follows :—Stout sheet aluminum, say about 1-16th of an inch in thickness, is cut into pieces an inch and a half square, and then the four corners are bent, for about a quarter of an inch, alternately up and down at right angles. This scheme prevents the pieces from lying flat against each other or upon the bottom of the beaker, and their washing is thus facilitated. The same pieces of aluminum may be used repeatedly, as they are but little attacked each time. Add 5 c.c. of strong sulphuric acid, cover the beaker, and heat to boiling. Boil strongly for about seven minutes. Unless the bulk of the solution is excessive, this will be quite sufficient with all percentages of copper. Ordinarily the aluminum will be found to be clean, and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Transfer the solution back to the original flask, and, by means of a washbottle of hot water, rinse in also as much of the copper as possible, leaving the aluminum behind. Drain the beaker as completely as possible, and temporarily set it aside with the aluminum, which may still retain a little copper. Allow the copper in the flask to settle, and then decant the liquid through a filter. Again wash the copper similarly two or three times with a little hot water, retaining it as completely as possible in the flask. Finally, wash the filter once or twice and endeavour to rinse all metallic particles down into the point. Now pour upon the aluminum in the beaker 5 c.c. of a mixture of equal volumes of strong nitric acid (1·42 sp. gr.) and water, and warm the beaker gently, but do not heat to boiling, as the aluminum would be thereby unnecessarily attacked. See that any copper present is dissolved, and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main portion of the copper. At this stage do not wash either the aluminum or the filter, but simply remove the flask and set the beaker in its place. Heat the mixture in the flask to boiling, and see that all the copper is dissolved. Then add about half a grm. of potassium chlorate, and again boil for a moment. This is to oxidise any arsenic present to arsenic acid, and is a very important point. Remove the flask from the lamp, and again place it under the funnel and wash the beaker, aluminum and filter with as little hot water as possible. Again boil sufficiently to remove every trace of red fumes. All the copper is now in the flask as nitrate. Add the zinc acetate, and proceed from this point precisely as described with the original nitrate

of copper solution in the standardisation of the hyposulphite, finally calculating the percentage of copper present from the amount of standard hyposulphite required. One point, however, remains to be further explained. According to the equation previously given, half a grm. of pure copper requires 2·62 grms. of potassium iodide. While direct experiment shows this to be apparently true, yet it is found that with small percentages of copper, the reaction, when only the theoretical amount of potassium iodide is taken, is slow, and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is therefore best to use not less than 3 grms. of potassium iodide in any case. An excess does no harm. Silver does not interfere with the method. Lead and bismuth are without effect, except that by forming yellowish iodides they may mask the end-point before adding starch. Lead is practically removed as sulphate at a previous stage. If bismuth is suspected in any appreciable amount, simply add the starch earlier in the titration. Arsenic when oxidised as described has no influence. The return of the blue tinge in the liquid by long standing after titration is of no significance; but a quick return of the colour, which an additional drop or two of the hyposulphite does not permanently destroy, may indicate either an incomplete combination of all the nitric acid with zinc, or a failure to completely boil off the red fumes when dissolving the copper in nitric acid. The assay in such a case is spoiled. This trouble may be avoided by carefully following the directions given, and not guessing at strengths or quantities. The amount of zinc acetate recommended is a safe excess. Sodium acetate does not appear to work as satisfactorily.

For the assay of alloys, &c., the necessary modifications of the foregoing scheme are obvious.

The foregoing scheme directs the use of 5 c.c. of dilute nitric acid for dissolving the copper previous to titration, and prescribes 6 to 7 grms., or about 20 c.c., of a saturated solution of zinc acetate as a safe excess of neutralising agent. It is obvious that if most of the nitric acid be boiled away, the amount of zinc salt necessary is greatly reduced. In such a case, however, it is perhaps best, for safety's sake, not to use less than one-half the prescribed quantity. Half the zinc salt may thus be saved at the expense of a little more time. This is the ordinary practice in my own laboratory.—*Journal of the American Chemical Society*, vol. xviii., No. 5.

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## A HYPOTHESIS ON THE ATOMIC MOTION OF THE ELEMENTS AND ON THEIR ORIGIN.

By FLAVIAN FLAVIZKY.

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THIS paper requires the five accompanying figures. The main proposition of the hypothesis is :—" The atoms of each element describe closed curves, which lie in planes respectively parallel and having a constant absolute position in space. The atoms of different elements move in planes which form with each other definite constant angles.

My hypothesis explains, not only the essential phases of chemical affinity, especially elective affinity and valence, but the periodic law itself is deduced as the consequence of a periodic change of the positions of the planes of atomic movements occurring with the increase of atomic weight.

This hypothesis is very closely connected with the question of the formation of the elements. If we assume the existence of a primitive matter, we must regard the elements as originating by an aggregation of the primitive matter. In this formation of the elements the primitive matter lost in part its motive energy. The atoms of the primitive matter, which in the beginning moved in the

most various directions, received a more regular motion in definite plane tracks. Such an orientation of movement could not take place under the influence of gravitation; we must suspect the action of a selective dualistic force, such as we meet in the phenomena of electricity.

In fine, I must make some remarks on the new elements which do not adapt themselves to the periodic system. Between the elements which follow the periodic law we always find elements with opposite properties, since most inactive nitrogen combines directly with boron, titanium, &c.; the recently discovered elements helium and argon appear more inactive than nitrogen. The peculiarities of the new elements depend perhaps on the character of their atomic movements not possessed by the ordinary components of the movements of other elements.

Hence we must conclude that helium and argon must have originated under different conditions, since their atomic motion takes place, not in closed curves, but perpendicularly to a plane the position of which may be regarded as intermediate among the positions of the planes of motion of the most energetic elements, such as the alkaline metals and the halogens. In this peculiarity of atomic motion we have perhaps the reason why the law of the entire rational relations of the atoms does not hold good for the new elements.—*Zeitschrift für Anorg. Chemie*, xii., Part 3, p. 182.

# A STUDY OF THE ZIRCONATES.*

### By F. P. VENABLE and THOMAS CLARKE.

(Concluded from p. 44).

## IV. *Fusion of Zirconia with Chlorides.*

THIS method was used by Hiortdahl in preparing the zirconates of magnesium and calcium, and by Ouvrard for the same, and also for strontium, barium, and lithium. According to the latter they all gave zirconates of the form $M_2ZrO_3$.

1. *Fusion with Sodium Chloride.*—There appeared to be very little action. The fusion was washed with water until free from chlorine. It was then treated as in the case of the carbonates. When 2 grms. of zirconia were fused with 16 grms. of sodium chloride, it was found that less than 2 per cent had been dissolved. In a second experiment, after heating six hours, the amount dissolved was less than 2-10ths of a per cent.

2. *Fusion with Potassium Chloride.*—No action was observable. When 2 grms. of zirconia were heated a number of hours with an excess of potassium chloride, and the mass then treated as above, only 3-10ths of a grm. had been acted upon. There seemed to be even less action in the case of lithium chloride at the temperature attainable by means of an ordinary water-blast lamp.

3. *Fusion with Alkaline Earths.*—Two attempts were made to prepare magnesium zirconate by fusing zirconia with magnesium chloride and ammonium chloride. It was not possible to prevent decomposition of the magnesium chloride. There seemed to be some action, but much difficulty was experienced in separating the products. The method described by Ouvrard gave evidences of zirconium in the washings.

In the case of fusions with calcium chloride no action could be observed. Two experiments were made, following closely the directions of Ouvrard, except as to temperature possibly, as to which no exact directions were given. A water-blast lamp was used for several hours. After leaching and washing, the mass left behind gave no zirconium to hydrochloric acid.

Our experiments with the chlorides have led us to believe that there is little or no action between zirconia and the chlorides of the alkalies or alkaline earths, except

where these chlorides are decomposed by the heat and oxides formed. Any action noticed is to be attributed to the oxides.

## V. *Precipitation from the Solution of a Zirconium Salt by means of an Alkaline Hydroxide.*

Watts speaks of this method, but no experiments are recorded. It seemed to us, upon examination of the question, that very little evidence as to the existence of the zirconates or their properties could be drawn from such a method of preparation as this. It has been repeatedly observed that the precipitate formed by means of ammonium hydroxide is extremely hard to wash free from ammonia. After a very large number of washings, however, it is practically free from ammonia. The same is true of sodium and potassium hydroxides. Is it to be inferred that a definite zirconate is precipitated? At what point shall the washing be stopped, for manifestly some washing is necessary? Equally it cannot be decided because of this loss of alkali by prolonged washing, that we have a decomposition of the zirconate caused by the action of the water. It therefore seemed to be quite useless to make analyses of the precipitates gotten with different degrees of washing,—especially as somewhat similar experiments were carried out under the next heading.

## VI. *The Solution of Zirconium Hydroxide in Caustic Alkali.*

It was found that zirconium hydroxide was perceptibly soluble in solutions of potassium and sodium hydroxide. Experiments were first made with a view of determining the extent of this solubility. Solutions of the two alkalies were made up of different strengths, an excess of zirconium hydroxide added, and the solution then boiled. After cooling, a measured quantity of the solution was drawn off, and the amount of zirconia present determined.

|  |  |  |  |  | Grm. |
|---|---|---|---|---|---|
| A 50 p. c. solution potassium hydroxide dissolved | | | | per c.c. | 0·00233 |
| 33 | ,, | ,, | ,, | ,, | 0·00097 |
| 25 | ,, | ,, | ,, | ,, | 0·00075 |
| 12 | ,, | ,, | ,, | ,, | 0·00009 |

In the case of sodium hydroxide there seemed to be a stronger solvent action:—

|  |  |  |  | Grm. |
|---|---|---|---|---|
| A 33 per cent solution dissolves per c.c. | | | | 0·00245 |
| 25 | ,, | ,, | ,, | 0·0012 |
| 12 | ,, | ,, | ,, | 0·0005 |

If a concentrated solution of alkali, saturated with zirconium hydroxide, is diluted, a portion of the zirconium will be precipitated. Neutralisation with acid will also cause a precipitation of the zirconium. In both cases alkali is retained by the precipitate in spite of washing. Analyses were made of some of these precipitates after very thorough washing (in no case was less than a litre of water used). The results in four experiments were sufficient to show that these precipitates were practically zirconium hydroxide with a varying percentage of alkali, this percentage ranging from 1·15 to 3·94. It is possible to assume that zirconates were formed, and then decomposed by the action of the water during the washing; but it seems more probable that this is, as is true in the case of so many hydroxides precipitated by alkaline hydroxides, merely a stubborn retention of alkali. Assuming that the strong alkaline solutions held zirconates in solution, attempts were next made to prepare other zirconates by precipitation from them.

The addition of solutions of various salts gave small precipitates which seemed to be formed mainly because of the dilution of the alkaline hydroxide, and to consist almost entirely of zirconium hydroxide. It was necessary, therefore, to use strongly alkaline solutions of the compounds of the elements to be experimented with,

This greatly diminished the choice of compounds. Concentrated solutions of aluminum and zinc hydroxides in potassium hydroxide gave precipitates, but they were in too small amounts for reliable analyses to be made.

Summing up the results of the experiments performed, it is clear that the method yielding the best results for the preparation of the zirconates is fusion of gently dried zirconia with hydroxides or prolonged heating with the oxides. In the case of the alkaline earths this yields zirconates containing one equivalent of each oxide, as $CaO.ZrO$, &c. The same is true of the magnesium compound. For lithium the compound obtained was $LiO.ZrO$. For the alkalies it seemed to be possible to obtain only zirconates having a largely preponderating proportion of zirconia. There seems to be a tendency toward the formation of distinct compounds under certain conditions. These polyzirconates, and the lithium compound also, may be decomposition products due to the action of the water used in leaching: No other mode of separation from the products of the fusion could be devised by us, however. If they are produced by the decomposing and solvent action of the water, it is a little strange that a point should be reached beyond which the leaching extracted no more alkali, and that this point varied with changed conditions. This is not the case where zirconium hydroxide has been precipitated by an alkali.

### Double Zirconates.

Two attempts at the formation of double zirconates were made.

1. *Potassium Calcium Zirconate.* — About 2 grms. each of zirconia, potassium hydroxide, and lime were heated together for about four hours. There was evidence of considerable action. The mass was treated with dilute acetic acid and thoroughly washed. Then, on treatment with dilute hydrochloric acid, nearly the whole residue went into solution. The analysis gave $ZrO_2$, 67·21 per cent; $CaO$, 31·06; $K_2O$, 1·11. This is a calcium zirconate ($CaO.ZrO_2$), with a small part of the CaO substituted by $K_2O$.

2. *Potassium Aluminum Zirconate.* — Two grms. of zirconia were fused for eight hours with 2 grms. of potassium hydroxide and 3 grms. of alumina. The mass was washed with dilute acetic acid until no more alumina was dissolved. The residue was treated with dilute hydrochloric acid, and the insoluble portion removed by filtration. The analysis gave $ZrO_2$, 72·38 per cent; $Al_2O_3$, 7·66; $K_2O$, 20·00. These experiments indicate the possible existence of double zirconates, and when time admits this point will be further examined.

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## THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.*

By HENRY FAY.

### Historical.

THE early history of photo-chemical reactions is involved with the history of photography. Schulze, in 1727, proved experimentally that the darkening of silver salts is due to the action of light; and, in 1799, Scheele ("Traité de l'Air et de Feu") showed the effects of different parts of the spectrum. It had been noticed several centuries before that silver salts are subject to change, but the work of Schulze was the first conclusive evidence that this change is due to the action of light. In the early part of this century the action of light on plant growth was studied by many investigators who received the incentive from a suggestion made by Priestley.

Certain physical phenomena were early noticed, as the effect on crystallisation by Petit (*Mém. de Paris*, 1722), who showed, in 1722, that solutions of potassium nitrate and ammonium chloride crystallise more readily in the sunlight than in the dark. These effects were studied more carefully by Chaptal (*Journ. de Phys.*, vol. xxxiv.) and Dize ("Sur la Crystallisation, &c.," 1789). In 1848, Becquerel (*Ann. Chim. Phys.*, [3], ix., 257) published his excellent researches on the phosphorescence of the sulphides of barium, calcium, and strontium, but none of these researches threw any light on the chemistry of the reactions caused by sunlight. Photography was being developed in the early part of the century and various effects were noticed, but the chemistry involved was not worked out. During this period many inorganic salts were found to undergo some change when exposed to the sunlight, and in general this change was a reduction, especially if there was an oxidisable organic substance present.

Among the salts most extensively studied were those of uranium. Before taking up the study of the reactions involved when uranium salts are decomposed in the sunlight, it will be well to review the work which has been done on the organic substances which are subject to change when exposed to the light. Many observations have been recorded in which the fact is simply stated that certain substances are sensitive to light, but only in a few cases has the reaction been a clear one. In the cases studied the reactions can be classified under one of these three heads—substitution, direct combination, and polymerisation.

Dumas (*Ann. Chim. Phys.*, [2], lxxiii., 77) has shown that the hydrogen atoms of the methyl group in acetic acid can be replaced by chlorine when the two substances are brought together in the direct sunlight, forming a substituted acetic acid. Phenomena of a similar nature were brought out by Schramm (*Ber. d. Chem. Ges.*, xviii., 350, 606, 1272; xix., 212), who has shown that when aromatic hydrocarbons having a side chain are treated with chlorine in the direct sunlight the substitution always takes place in the side chain.

Under the second head come the researches of Cahours (*Compt. Rend.*, xxiii., 1070), who prepared perchlormethyl oxalate and formate by bringing together the acids and alcohol in presence of chlorine. When exposed to the sunlight, the reaction takes place, forming the ethereal salts.

Chastaing (*Ann. Chim. Phys.*, [5], xi., 145) exposed acetic and butyric acids with alcohol, and by means of titration was able to measure the rate of etherification.

Somewhat similar are the facts discovered by Klinger (*Ann. Chem.* (Liebig), ccxlix., 137), who showed that aldehyds have the power of combining with phenanthrene-quinone. He also noticed that if a reducible substance is exposed to light in presence of an oxidisable one, the solvent is oxidised while the substance in solution is reduced. By this means Klinger was able to convert phenanthrenequinone into phenanthrenehydroquinone, and at the same time the solvent, ether, was oxidised to acetic aldehyd. He found that benzil in ether solution passed over into a substance which he called benzil-benzoïn, on account of the ease with which it can be broken down into these two substances. He represents the decomposition by the equation—

$$C_{42}H_{32}O_6 = 2C_6H_5.CO.CO.C_6H_5 + C_6H_5.CHOH.CO.C_6H_5$$
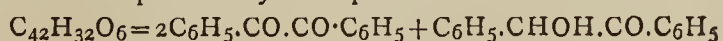
Under the head of polymerisation come the facts discovered by Lemoin (*Compt. Rend.*, xciii., 514). He found that chloral and styrolene are polymerised when exposed to the sunlight. Similar facts have been noticed in the field of inorganic chemistry, as in the case of phosphorus and sulphur. Yellow phosphorus is converted into the red modification, and a solution of sulphur in carbon bisulphide deposits the insoluble modification.

The work of Tyndall (*Proc. Roy. Soc.*, xvii., 92, 104) on light reactions cannot be placed under any of these heads, as the nature of the reaction is not known. He exposed the vapour of amyl nitrite to a beam of light and found that there was decomposition; oxides of nitrogen were formed, but the other products were not examined. Tyndall also found that allyl iodide and isopropyl iodide are affected by light, but he did not study the subject from its chemical side.

Oxalic acid has been extensively used in photo-chemical reactions, especially in form of its salts, and it has been recommended as a means of determining the amount of sunlight. Döbereiner (*Schweigger's Journ.*, lxii., 90) proposed to use ferric oxalate as a photometer in which the ferrous oxalate or the carbon dioxide given off could be measured. He also found that oxalic acid will reduce platinum chloride to metal, and that silver oxalate is partially reduced to metal.

Eder (*Wein. Academy Ber.*, ii., 1879) used as a photometer a solution of ammonium oxalate and mercuric chloride, which, on exposure to sunlight, gives off carbon dioxide and deposits mercurous chloride according to the equation—

$$2HgCl_2 + (NH_4)_2C_2O_4 = 2HgCl + 2NH_4Cl + 2CO_2.$$
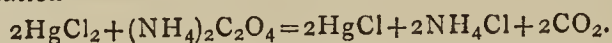
Having reviewed briefly the effects of light on certain organic substances, the history of the reactions which involve the use of uranium salts will be given in detail. The first person to find that uranium salts are sensitive to light was Bucholz (*Ann. Chim. Phys.*, [1], lvi., 142), who described (1805) certain effects produced by the sulphate and alcohol. He says:—"Uranium sulphate dissolves in 25 parts of alcohol, and the solution undergoes remarkable changes on exposure to the sunlight; the yellow liquid becomes turbid and deposits a greyish green substance. After several days exposure the solution acquires an odour of nitric ether; the filtrate is colourless and contains no uranium; the precipitate of a green colour and retains sulphuric acid." Bucholz further observes that an ether solution of uranyl nitrate becomes green on exposure to sunlight, and a black substance is deposited.

Chemists added little to these results until Ebelman (*Ann. Chem.* (Liebig), xliii., 294), in 1831, took up the subject. He confirmed the results of Bucholz with the uranium sulphate and alcohol, but noticed in addition that green crystals were formed, which he said were uranium protoxide. The precipitate he called the bibasic sulphate of the protoxide, and gave it the formula $2UO.SO_3 + 2H_2O.$

Uranium oxalate was also investigated by Ebelman. He observed that a solution of uranyl oxalate decomposed into a brown substance, which he believed to be the hydrated oxide, and into carbon dioxide and carbon monoxide in changing proportions.

St. Victor and Corvissart (*Compt. Rend.*, xxi.; *Ann. Chem.* (Liebig), xliii., 114), working on the action of light on organic substances, noticed that if a solution of oxalic acid is exposed to the light it will quickly reduce a gold solution. They heated to boiling a 4 per cent solution of oxalic acid with a 1 per cent solution of uranyl nitrate, finding that in the dark no decomposition would take place, but after exposing to the sunlight action soon began. They say that carbon monoxide was given off, but do not mention having obtained any carbon dioxide. Another fact of interest discovered by them was that a small quantity of uranyl nitrate increased ten-fold the action of light on any amylaceous matter, converting it into dextrin and glucose.

Seekamp (*Ann. Chem.* (Liebig), cxxii., 113) repeated the work of St. Victor and Corvissart, and found that after a solution of uranyl nitrate and oxalic acid had been exposed to the light for some time there was a deposit of a green crystalline powder; the solution became colourless and showed an acid reaction. The acid was identified as formic acid by means of its lead and barium salts.

From succinic acid he obtained carbon dioxide and propionic acid, and the precipitate which was formed he believed to be uranous succinate. Butyric acid and carbon dioxide were obtained from pyrotartaric acid.

H. C. Bolton (*Am. Journ. Sci.*, [2], xlviii., 206) in a review of the work done on uranium salts in photo-chemical reactions, adds some interesting facts discovered while working with certain uranium salts in photographic processes. He obtained a salt which is the double oxyfluoride of uranium and potassium, having the composition represented by the formula $2UO_2F + 3KF$. A solution of this salt acidified with formic acid decomposes in the sunlight, forming a precipitate which gives the formula $4UF + KF$. Oxalic acid causes a similar reduction, but with the formation of Ebelman's violet hydrate. Solutions of the nitrate, sulphate, oxychloride, and oxyfluoride are reduced when mixed with glycerin and placed in the sunlight. Even in the dry state, the uranium-ammonium citrate was found to be sensitive to light.

Wisbar (*Ann. Chem.* (Liebig), ccxxxii., 262) next took up the study of light on uranium salts. He verified Seekamp's work on pyrotartaric acid, and showed, in addition, that butyric acid in presence of uranium salts breaks down into propane and carbon dioxide.

Somewhat similar to the work of Wisbar is that of Louis Lucien Bonaparte (*J. Prakt. Chem.*, xxx., 308), who obtained a decomposition of valeric acid by exposing it with a solution of uranyl valerate. The products formed he believed to be uranous valerate, and gases which he believed to be carbon dioxide, carbon monoxide, and a hydrocarbon.

Chastaing (*Ann. Chim. Phys.*, [5], xi., 145) studied the effect of the red and violet rays of the spectrum on solutions of uranyl nitrate and alcohol, and noticed the odour of aldehyd, which is probably the odour Bucholz took for *nitric ether*. Some uranyl acetate was formed in the solution.

At the suggestion of Prof. Remsen, H. C. Jones, working in this laboratory, undertook some time ago the study of the action of light on oxalic acid in the presence of uranium salts. As the results of his work have not been published, a short account of the results which he obtained will be given.

He verified the statement of Seekamp that, in the presence of uranium oxalate, oxalic acid is broken down into carbon dioxide, carbon monoxide, and formic acid. The equation given by Seekamp to express the reaction is—

$$UO_2(C_2O_4) + 2H_2C_2O_4 = U(C_2O_4)_2 + 2CO_2 + 2H_2O.$$
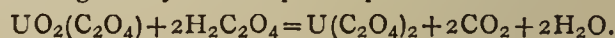
Seekamp (*Ann. Chem.* (Liebig), cxxii., 115) thought that the green compound precipitated was uranous oxalate, of the composition $U(C_2O_4)_2.6H_2O$.

A series of experiments was made by Jones in which varying amounts of uranyl oxalate and oxalic acid were used. The amount of carbon dioxide found in every case agreed to within a few c.c. with the amount of carbon dioxide which would have been liberated from the oxalic acid used, had it decomposed directly into carbon dioxide, carbon monoxide, and water. The amount of carbon monoxide set free, plus the amount combined as formic acid, was always somewhat less than the carbon dioxide.

The composition of the precipitate formed was found to depend on the amount of uranyl oxalate relatively to the free oxalic acid originally used. In all cases where a very large excess of oxalic acid was not used, it could be clearly seen that the precipitate was a mixture of crystals and an amorphous mass.

Analyses of the precipitate formed from various mixtures confirmed the belief that the precipitate was a mixture. When a solution containing 3 grms. of uranyl oxalate and 30 grms. of oxalic acid had been exposed to the light for a time, it was noticed that green crystals were forming on the bottom and sides of the flask. The solution was then removed from the direct sunlight, and allowed to stand in diffused light for some time, when a

considerable quantity of the crystals was obtained free from impurities. An analysis of the crystals dried between filter-paper gave 45·05 per cent uranium, which agreed fairly well with the composition $U(C_2O_4)_2.6H_2O$, which requires 45·8 per cent of uranium, on the basis $U = 240$, $C = 12$, $O = 16$.

Finally, a solution was prepared containing 3 grms. uranyl oxalate and 45 grms. oxalic acid. Pure crystals were obtained, as described above, which contained 46·05 per cent of uranium. It thus appears that the crystalline compound is formed pure only when a very large excess of oxalic acid is used.

It was then hoped that, by using a large amount of uranyl oxalate relatively to oxalic acid, the amorphous compound might be obtained in pure condition. For this purpose a solution containing 2 grms. of uranyl oxalate and 2 grms. of oxalic acid were exposed to the light. A greenish mass was at first precipitated, which, on longer exposure, became purplish brown. A solution of uranyl oxalate exposed alone to the direct sunlight apparently underwent the same transformation.

It was found, further, that a very small amount of uranyl oxalate will decompose a very large, if not an unlimited, amount of free oxalic acid if exposed *continuously* to the direct sunlight. If not continuously, the crystalline compound will separate out of the solution and the action will cease. Thus the reaction suggested by Seekamp, and given above, cannot express the whole truth, since, according to it, one molecule of uranyl oxalate can decompose only two molecules of free oxalic acid.

The uranyl salt seems to act in some way as an oxidising agent, as is indicated by the fact that the product precipitated is some reduction-product of the uranyl compound originally used.

### Decomposition of Oxalic Acid in the presence of Uranyl Oxalate.

As the nature of the precipitate formed when oxalic acid is exposed to the sunlight in presence of uranyl oxalate was not cleared up by Jones on account of lack of time, it was decided, at Prof. Remsen's suggestion, to continue the work and study the products of decomposition. For this purpose, solutions containing oxalic acid and uranyl oxalate in varying proportions were exposed to the direct sunlight, and in all cases it was found that after considerable gas had been given off the solution became cloudy, and then deposited a light green crystalline powder. When all the oxalic acid was decomposed, and the evolution of gas had ceased, the remainder of the uranium in solution was deposited as a flocky purplish brown substance. Evidently, concordant results could not be obtained by working with the precipitate as a whole, and it was decided to remove the light green coloured precipitate when first formed.

To obtain it, 3 grms. uranyl oxalate and 2 grms. oxalic acid were dissolved in a litre of water, and exposed to the direct sunlight. When some of the green precipitate first formed had settled to the bottom of the flask it was filtered off, washed with water, and then dried between filter-papers. The dry substance has a very pale green colour, and showed no tendency to oxidation or change of any kind.

The uranium was determined by heating the substance in a porcelain crucible and weighing as the oxide $U_3O_8$. In all of the analyses made this method was used; frequently, however, the oxide formed was converted into the nitrate, and the nitrate again decomposed. This was done simply to control the results, as the oxide $U_3O_8$ is more readily formed from the nitrate than from the uranium salt of organic acids.

The green-coloured substance gave these results :—

I. 0·2637 grm. substance gave 0·1776 grm. $U_3O_8 = 57·17$ per cent U.

II. 0·2015 grm. substance gave 0·1369 grm. $U_3O_8 = 57·68$ per cent U.

III. 0·2560 grm. substance gave 0·1725 grm. $U_3O_8 = 57·20$ per cent U.

Calculated for $U(C_2O_4)_2$, 57·69 per cent U.

This shows the substance to be uranous oxalate. It can be obtained at any time, provided the solutions be continuously exposed to the sunlight, and not too large an excess of oxalic acid be present. It was shown by Jones that when a large excess of oxalic acid is present, and the solution removed after a short exposure to the light, there is a strong tendency to the formation of the crystalline product $U(C_2O_4)_2.6H_2O$. If the solutions are exposed until all of the oxalic acid is decomposed, some of the purplish brown substance is then formed.

Desiring to obtain the purplish brown precipitate in pure condition, several attempts were made to get it from solutions containing oxalic acid and uranyl oxalate by removing the uranous oxalate formed and subsequent exposure, but in all cases the precipitate contained a mixture of the two precipitates. When uranyl oxalate in solution is exposed to the sunlight, the same purplish brown precipitate is formed, and it was decided to use the uranyl oxalate alone for the purpose of obtaining it.

### Decomposition of Uranyl Oxalate.

Four grms. of uranyl oxalate were dissolved in a litre of water, and the solution filtered to get rid of a small amount of undissolved substance. The solution was exposed to direct sunlight, and within five minutes after exposure the clear yellow solution had become cloudy. The cloudiness increased rapidly. In half an hour there was a deposit of the purplish brown substance on the bottom and side of the flask nearest the source of light. There was no evolution of gas.

Thinking that possibly the solution held the gas, several attempts were made to collect any gas formed by attaching large tubes filled with uranyl oxalate solutions to nitrometers containing mercury. Under much reduced pressure, and even by gentle heating, it was impossible to collect any gas. The precipitate formed in the above solutions was filtered off, washed with water, and left to dry in the air. The brown substance on drying changed to yellow, so that it was impossible to prepare it in this way for analysis. Even on drying rapidly between filter-papers there was some change noticed. If the brown substance is allowed to stand in the flask in which it is precipitated the same change takes place, although not so rapidly. The filtrate was always neutral to litmus, and contained nothing but traces of uranium salts, which were thrown out on evaporation to small volume. It was impossible in any case to get the uranium precipitated entirely, although the portion remaining in solution was extremely small in comparison with the whole amount of uranium present.

(To be continued).

Royal Institution. — A General Monthly Meeting of the Members of the Royal Institution was held on July 6th, Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members :—The Right Hon. Lord Windsor, Mr. Herbert Page, F.R.C.S., and Mr. Alfred Suart.

City and Guilds of London Institute.—The Executive Committee of the City and Guilds of London Institute have appointed Mr. W. E. Dalby, since 1891 University Demonstrator of Mechanism and Applied Mechanics at Cambridge, to the Professorship of Mechanics and Applied Mathematics at the Institute's Technical College, Finsbury, rendered vacant by the resignation of Prof. Perry. Mr. Dalby served a seven years apprenticeship in the locomotive works of the Great Eastern Railway and gained a Whitworth Scholarship in 1883. In 1884 he entered the service of the London and North Western Railway, graduated B.Sc. London in 1890, and in 1894 received the full degree of M.A. *honoris causâ* from the University of Cambridge.

## ALUMINUM ALCOHOLATES.

### By H. W. HILLYER.

IN work preparatory to using the method of Wislicenus and Kaufmann (*Ber. d. Chem. Ges.*, xxviii., 1323) for reduction in neutral solutions by use of amalgamated aluminum, observations were made which have led to the work of which this is a preliminary notice.

According to these authors amalgamated aluminum does not act on absolute alcohol, but can be preserved for use covered by absolute alcohol. By following their directions we obtained an amalgam having properties like those described; but in order to avoid all contact with the air and the degeneration of the amalgam, caused by its coating over with hydroxide, instead of an aqueous solution of mercuric chloride, a solution of mercuric chloride in absolute alcohol was used. When this was brought in contact with chipped aluminum an evolution of gas soon commenced, and instead of ceasing, as might have been expected, when the little water in the alcohol had been decomposed, it increased in rapidity, and the alcohol became heated nearly or quite to the boiling-point.

The action gradually became more moderate, but continued so long that on cooling the whole gelatinised. The most probable reaction is—

$$Al + 3C_2H_6O = Al(OC_2H_5)_3 + 3H.$$

Knowing from the work of Gladstone and Tribe that aluminum alcoholates, in contrast to all other known alcoholates, can be distilled under diminished pressure, an attempt was made to distil the product obtained. After the alcohol, a grey distillate of mercury came over under 20 m.m. pressure, and then white fumes and an oily liquid solidifying in the receiver. The distillate contains much aluminum, but is greatly contaminated with mercury.

In the attempt to avoid the presence of mercury, which made the purification difficult, other salts soluble in alcohol were tried, but with no special result until, on using fuming stannic chloride, a reaction took place similar to that with the mercuric chloride. In this case spongy tin separated, a gas was rapidly evolved, and the liquid became quite hot. In both cases an application of external heat starts a new evolution of gas. When no more gas was evolved the alcohol was distilled off and the residue in the retort subjected to distillation under diminished pressure. A distillate was obtained rich in aluminum and containing no tin. Determinations of the amount of aluminum seemed to indicate that the substance might be aluminum hydroxydiethylate, $Al(OC_2H_5)_2OH$, but work on the action of ethyl alcohol was temporarily interrupted at this point. Two experiments with methyl alcohol gave good evolution of gas, but no substance could be distilled under a diminished pressure. The retort after distilling off the alcohol contained apparently nothing but aluminum oxide or hydroxide. Work with normal propyl alcohol has resulted in showing definitely that aluminum tripropylate is formed under similar conditions. An account of this work will soon be published in detail.

Isopropyl and amyl alcohol also react on aluminum in the presence of aluminum chloride and the spongy tin formed by its action on stannic chloride in solution in these alcohols. The aluminum is dissolved to give a solution from which it is precipitated, probably as hydroxide, on addition of water or by mere action of the moisture of the air.

The writer desires to reserve for the present the privilege of investigating the action of aluminum on alcohols to which mercuric chloride and stannic chloride have been added, and to investigate the action of sulphur dioxide and of hydrogen sulphide on the alcoholates thus formed. —*American Chemical Journal*, vol. xviii., No. 7.

## INTERNATIONAL CATALOGUE CONFERENCE.

THE following delegates attended:—

*Austria.*—Prof. Ernst Mach, Mitglied der Kaiserlichen Akademie der Wissenschaften, Vienna; Prof. Edmund Weiss, Mitglied der Kaiserlichen Akademie der Wissenschaften, Vienna.

*Belgium.*—M. H. La Fontaine, Membre de l'Institut International de Bibliographie, Brussels; M. Paul Otlet, Membre de l'Institut International de Bibliographie; M. de Wulf, Membre de l'Institut International de Bibliographie.

*Denmark.*—Prof. Christiansen, Universitet, Copenhagen.

*France.*—Prof. G. Darboux, Membre de l'Institut de France; Dr. J. Deniker, Bibliothécaire, Muséum d'Histoire Naturelle, Paris.

*Germany.*—Prof. Walther Dyck, Mitglied der K. Bay. Akad. der Wiss. zu München; Prof. Dziatzko, Direktor der Universitäts Bibliothek, Göttingen; Prof. van 't Hoff, Mitglied der K. P. Akademie der Wissenschaften zu Berlin; Prof. Möbius, Mitglied der K. P. Akademie der Wissenschaften zu Berlin; Prof. Schwalbe, Direktor, Berlin.

*Greece.*—M. Avierinos M. Averoff, Greek Consul at Edinburgh.

*Hungary.* — Dr. Theodore Duka, Membre Académie Hongroise des Sciences, Buda-Pesth; Prof. August Heller, Librarian, Ungarische Akademie, Buda-Pesth.

*Italy.*—General Annibale Ferrero, Italian Ambassador in London.

*Japan.*—Assistant Professor Hantaro Nagaoka, University, Tokio; Assistant Professor Gakutaro Osawa, Medical College, Tokio.

*Mexico.*—Señor Don Francisco del Paso y Troncoso.

*Netherlands.*—Prof. D. J. Korteweg, Universiteit, Amsterdam.

*Norway.* — Dr. Jörgen Brunchorst, Secretary, Bergen Museum.

*Sweden.*—Dr. E. W. Dahlgren, Librarian, Kongl. Svenska Vetenskaps Akademie, Stockholm.

*Switzerland.* — M. C. D. Bourcart, Swiss Minister in London; Prof. Dr. F. A. Forel, Président du Comité Central de la Société Helvétique des Sciences Naturelles.

*United Kingdom.*—Representing the Government: Right Hon. Sir John E. Gorst, Q.C., M.P., Vice-President of the Committee of Council on Education. Representing the Royal Society of London: Prof. Michael Foster, Sec. R.S.; Prof. H. E. Armstrong, F.R.S.; Mr. J. Norman Lockyer, C.B., F.R.S.; Dr. Ludwig Mond, F.R.S.; Prof. A. W. Rücker, F.R.S.

*United States.*—Dr. John S. Billings, U.S. Army; Prof. Simon Newcomb, For. Mem. R.S., U.S. Nautical Almanac Office.

*Canada.* — The Hon. Sir Donald A. Smith, G.C.M.G., High Commissioner for Canada.

*Cape Colony.*—Roland Trimen, Esq., F.R.S.; Dr. David Gill, F.R.S.

*India.*—Lieut.-General Richard Strachey, R.E., F.R.S.

*Natal.*—Walter Peace, Esq., C.M.G., the Agent-General for Natal.

*New South Wales.*—Prof. Liversidge, F.R.S.

*New Zealand.*—The Hon. W. P. Reeves, Agent-General for New Zealand.

*Queensland.* — Chas. S. Dicken, Esq., C.M.G., Acting Agent-General for Queensland.

OPENING MEETING, *Tuesday, July 14th, 1896, 11 a.m., at the Rooms of the Royal Society, Burlington House.*

1. Prof. Foster (Sec. R.S.) moved that Sir J. Gorst act as provisional President for the purpose of organising the Conference.

2. The resolution, having been unanimously accepted, Sir John Gorst welcomed the Delegates.

3. Prof. Armstrong gave a brief account of the work done by the Royal Society in arranging for the Conference, as well as of the work to be accomplished.

The following resolutions were then agreed to :—

4. That each delegate shall have a vote in deciding all questions brought before the Conference.

5. That English, French, and German be the official languages of the Conference, but that it shall be open for any delegate to address the Conference in any other language, provided that he supplies for the *procès verbal* of the Conference a written translation of his remarks into one or other of the official languages.

6. General Ferrero moved that Sir John E. Gorst be the President of the Conference. The motion having been unanimously accepted,

7. Sir John Gorst nominated as Vice-Presidents—General Ferrero, Prof. Darboux, Prof. Mach, Prof. Möbius, Prof. Newcomb.

It was further resolved :—

8. That Prof. Armstrong be the Secretary for the English language. That Prof. Forel be the Secretary for the French language. That Prof. Dyck be the Secretary for the German language.

9. That the Secretaries, with the help of shorthand reporters, be responsible for the *procès verbal* of the proceedings of the Conference in their respective languages.

10. That the Conference adjourn at 1 p.m., and re-assemble at 2.30 p.m., continuing the sitting not later than 5 p.m.

11. That on Wednesday the Conference meet at 10 a.m., adjourning as before from 1 p.m. until 2.30 p.m.

The resolutions prepared by the International Catalogue Committee of the Royal Society to serve as a basis for discussion were then taken into consideration, and the following resolutions were agreed to *nemine contradicente.*

12. That it is desirable to compile and publish by means of some international organisation a complete Catalogue of Scientific Literature, arranged according both to subject-matter and to authors' names.

13. That in preparing such a Catalogue regard shall, in the first instance, be had to the requirements of scientific investigators, to the end that these may, by means of the Catalogue, find out most easily what has been published concerning any particular subject of enquiry.

14. That the administration of such a Catalogue be entrusted to a representative body, hereinafter called the International Council, the members of which shall be chosen as hereinafter provided.

15. That the final editing and the publication of the Catalogue be entrusted to an organisation, hereinafter called the Central International Bureau, under the direction of the International Council.

16. That any country which shall declare its willingness to undertake the task shall be entrusted with the duty of collecting, provisionally classifying, and transmitting to the Central Bureau, in accordance with rules laid down by the International Council, all the entries belonging to the scientific literature of that country.

17. That in indexing according to subject-matter regard shall be had, not only to the title (of a paper or book), but also to the nature of the contents.

18. That the Catalogue shall comprise all published original contributions to the branches of science hereinafter mentioned, whether appearing in periodicals or in the publications of Societies, or as independent pamphlets, memoirs, or books.

SECOND MEETING, *Wednesday, July 15th,* 1896, 10 a.m., *at the Rooms of the Royal Society, Burlington House.*

19. It having been proposed—

That a contribution to science for the purposes of the Catalogue be considered to mean a contribution to any of the mathematical, physical, or natural sciences, the limits of the several sciences to be determined hereafter.—

The following amendment was moved, and, after discussion, adopted :—

That the terms of the resolution be referred to a Committee, consisting of Messrs. Armstrong, Billings, Darboux, Korteweg, Möbius, and Schwalbe, to report to the Conference at the opening meeting, on July 16th.

The following resolutions were then agreed to, *nemine contradicente :—*

20. That in each country the system of collecting and preparing material for the Catalogue shall be subject to the approval of the International Council.

21. That in judging whether a publication is to be considered as a contribution to science suitable for entry in the Catalogue, regard shall be had to its contents, irrespective of the channel through which it is published.

22. That the Central Bureau shall issue the Catalogue in the form of "slips" or "cards," the details of the cards to be hereafter determined, and the issue to take place as promptly as possible. Cards corresponding to any one or more branches of science, or to sections of such sciences, shall be supplied separately at the discretion and under the direction of the Central Bureau.

23. That the Central Bureau shall also issue the Catalogue in book form from time to time, the entries being classified according to the rules to be hereafter determined.

That the issue in the book form shall be in parts corresponding to the several branches of science, the several parts being supplied separately, at the discretion and under the direction of the Central Bureau.

24. General Ferrero having moved—

That the Central Bureau be located in London—

The resolution was seconded by M. Darboux, supported by Messrs. Möbius, Heller, Weiss, Simon Newcomb, Otlet, Duka, Bourcart, Dahlgren, and Korteweg, and accepted by acclamation.

THIRD MEETING, *Thursday, July 16th,* 1896, *at the Rooms of the Royal Society, Burlington House.*

The appointment of Prof. Liversidge, F.R.S., as official delegate representing New South Wales, was notified.

25. The following resolutions were agreed to *nemine contradicente :—*

That a contribution to science for the purposes of the Catalogue be considered to mean a contribution to the mathematical, physical, or natural sciences, such as, for example, mathematics, astronomy, physics, chemistry, mineralogy, geology, botany, mathematical and physical geography, zoology, anatomy, physiology, general and experimental pathology, experimental psychology, and anthropology, to the exclusion of what are sometimes called the applied sciences—the limits of the several sciences to be determined hereafter.

26. That the Royal Society be requested to form a Committee to study all questions relating to the Catalogue referred to it by the Conference, or remaining undecided at the close of the present sittings of the Conference, and to report thereon to the Governments concerned.

27. Since it is probable that, if organisations be established in accordance with Resolution 16, the Guarantee Fund required for the Central Bureau can be provided by voluntary subscriptions in various countries, this Conference does not think it necessary at present to appeal to any of the Governments represented at the Conference for financial aid to the Central Bureau.

FOURTH MEETING, *Friday, July 17th,* 1896, *at the Rooms of the Royal Society, Burlington House.*

The following resolutions were agreed to *nemine contradicente :—*

28. The Conference being unable to accept any of the systems of classification recently proposed remits the study of classifications to the Committee of Organisation.

The Belgian delegates expressly desired that it be

placed on record that they abstained from voting on this resolution.

29. That English be the language of the two catalogues, authors' names and titles being given in the original languages except when these belong to a category to be determined by the International Council.

30. That it be left to the Committee (of the Royal Society) to suggest such details as will render the Catalogue of the greatest possible use to those unfamiliar with English.

31. That it is desirable that the Royal Society should be informed, at a date not later than January 1st, 1898, what steps (if any) are being taken, or are likely to be taken, in the countries whose Governments are represented at the Conference, towards establishing organisations for the purpose of securing the end had in view in Resolution 16.

32. That the Delegates, in reporting to their respective Governments the Proceedings of the Conference, should call immediate attention to Resolutions 16 and 31.

33. That January 1, 1900, be fixed as the date of the beginning of the Catalogue.

34. That the Royal Society be requested to undertake the editing, publication, and distribution of a verbatim report of the Proceedings of the Conference.

35. That the *procès verbal* of the Conference be signed by the President and Secretaries.

36. That this Conference requests the Royal Society to express to my Lord Mayor of London and to Dr. L. Mond their grateful, hearty appreciation of the hospitality shown by them to the Delegates.

37. On the motion of M. Darboux, a vote of thanks to Sir John Gorst, for presiding over the Conference and his conduct in the chair, was passed by acclamation.

38. On the motion of Prof. Weiss, a vote of thanks to the Royal Society, for their cordial reception of the Delegates, was unanimously carried.

(Signed) { JOHN E. GORST, *President.*<br>HENRY E. ARMSTRONG,<br>WALTHER DYCK, } *Secretaries.*<br>F. A. FOREL,

# OBITUARY.

## THE LATE PROFESSOR AUGUST KEKULÉ.

THE 13th of the current month witnessed the death of August Kekulé—whose full name is Friedrich August Kekulé von Stradonitz.

This illustrious *savant* was born at Darmstadt in 1829, and was at first destined to become an architect. The lectures of Liebig induced him to turn his attention to chemistry. At Paris he was a pupil of Dumas, Wurtz, and Gerhardt. In London he met with Williamson, and became familiar with the more philosophic phase of our science.

In 1856 he became a privat docent of chemistry at Heidelberg. Two years later he succeeded to the chemical chair at Ghent; and in 1865 he succeeded A. W. Hofmann as Professor of Chemistry and Director of the Chemical Institute of the University of Bonn, an office which he filled up to his death.

His principal work, "Lehrbuch der Organischen Chemie" (Erlangen, 1861—1869) has not been completed, but like its companion work, "Chemie der Benzole derivale" (Erlangen, 1867), has contributed most essentially to the development of theoretical chemistry.—*Chemiker Zeitung.*

The Reward of Physical Research.—A mighty advertiser does honour to Prof. Röntgen by announcing the new X-rays camera as "the great joke of the day."

# NOTICES OF BOOKS.

*Incandescence by Gas and Petroleum. Acetylene and its Applications.* By F. DOMMER, Professor at the School of Industrial Physics and Chemistry of the City of Paris. Paris: Bernard Tignol.

THE author considers that the struggle between the electric light and its rivals is far from being decided. Pointing to the system of Siemens and Wenham, to the incandescence burners of Auer, and the complete consumption burners of Bandsept and Denayrouse, he has much to advance, as far at least as the price of the illuminant is concerned. As regards acetylene, everything must depend on the price at which its source, calcium carbide, can be put on the market. M. Dommer is sceptical as regards the alleged quotation of 150 francs per ton.

He remarks that the eye is most sensitive to the yellow and green rays; the luminous intensity in the yellow being 1000, that of the ultra-violet is only 6, and that of the ultra-red 0.

Lights rich in violet and ultra-violet rays, like those of magnesium and the arc, are hurtful to the sight. These rays, in sunlight, occasion sun-stroke, or erythema, and contribute to the destruction of the fibres of the crystalline lens. Hence the production of violet rays, in sources of artificial light, should therefore be avoided.

Lights very rich in yellow rays tend to destroy the erythropsine, which is re-formed in darkness.

If we wish to distinguish forms we must adopt a reddish lantern rather than one giving a yellow light.

The ideal source of light would emit neither thermic radiations nor dark rays.

It is here declared that the final optical yield of the energy expended in an electric lamp is only about 1 per cent.

It is an interesting fact that the light of the firefly (*Lampyris*) consists almost exclusively of yellow and green rays.

The photometers of Rumford, Bunsen, and Foucault are described and figured in Chapter IX., as also the standards officially adopted in different countries. The carcel is still employed in France, as is the spermaceti candle in Britain. It is remarked, truly enough, that this standard is liable to vary to the extent of 30 per cent. The pentane standard is not criticised. Germany employs the paraffin standard candle, and the amyl-acetate lamp invented by Von Hefner-Alteneck.

The absolute unit, proposed by Violle, is the luminous intensity emitted in the normal direction by a square centimetre of platinum in the temperature of solidification. It is equal to 2·08 carcel. The international unit, or "decimal candle," is the 1-20th of Violle's unit, and, like all candles, is liable to fluctuale. On the faith of experiments made in Paris, the Auer burner would appear more economical than the electric light, though a gas incandescence system would be still less expensive.

The second part of the work is devoted to acetylene, $C_2H_2$, a compound discovered by Ed. Davy in 1836, and produced synthetically by Berthelot. The preparation of calcium carbide, on such a scale that it can be applied to the production of acetylene, seems due to Moissan and his assistant, Bullier.

Acetylene is a colourless gas with an odour of garlic, but agreeably ethereal if prepared from pure material. If a small primer of mercury fulminate is made to explode in the midst of this gas, it is decomposed with a violent explosion and a large flame.

It produces in equal volumes sixteen times more light than Paris gas burning in a normal Bengel burner. The amount of heat given out is, however, relatively less.

Berthelot has established that acetylene is an endothermic substance. If diluted with atmospheric oxygen it forms very dangerous explosive mixtures. It is very

apt to strike back into the mains or into the gasometers. To avoid this danger, the acetylene is diluted with nitrogen. The maximum explosive power is obtained with a mixture of 12 parts of air to 1 part of acetylene.

Acetylene is not more poisonous than the ordinary carbides forming ethylene, &c., or than coal-gas.

Coal-gas may be enriched by adding small quantities of acetylene not exceeding 5 to 6 per cent. At the price of 50 centimes per cubic metre acetylene may enter into practical use at gas-works.

The work before us is valuable as calling the attention of industrialists to a product which has possibly a great future.

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*An Inquiry into the Alleged Liability of Wood Charcoal to Spontaneous Combustion.* Cartvale Chemical Co., Limited, Paisley. Third Edition, Revised. Paisley and London: Alex. Gardner.

THE question here discussed is one of serious moment. If charcoal is, under unknown or undefined circumstances, capable of spontaneous explosion, the manufacture, carriage, and storage of gunpowder, *i.e.*, the old black powder, is attended with a source of danger not sufficiently appreciated.

It is, of course, necessary to note the exact sense of the term used in this discussion. The Cartvale Co. conclude from their own experiments and observations, as well as from correspondence with experts, that :— " Freshly made charcoal, *i.e.*, charcoal which has not absorbed its moisture and oxygen, is liable to so-called spontaneous combustion or re-ignition. After having absorbed its moisture and oxygen, which it does in the course of a few days, it is never liable to so-called spontaneous combustion." With this conclusion our own observations allow us to agree.

The Cartvale Chemical Co. prudently and justly confine their conclusion to wood-charcoal, with which alone they are practically concerned.

Bone-black, or animal charcoal, is much more liable to heating, and may even in chemical manures and composts give rise to actual combustion. Thus " spent " animal charcoal, though perfectly cool, and by no means absolutely free from moisture, and though largely mixed with mineral matter, has been known to " heat." From the point of view of fire insurance companies, spontaneous combustion comprises not only combustion from causes inherent in the material, but combustion arising from contact with oils water, acids, &c. ; bulls'-eye windows and sun's rays converting these into magnifying (better, " burning ") glasses ; cotton-wool, greasy rags, &c., in mills.

If we remember the extreme liability of ground dyewoods to heat, we shall see that the question is not absolutely exhausted. These points, however, lie outside the purview of the charcoal burner and gunpowder manufacturer.

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*Chilian Review of Hygiene.* ("Revista Chilena de Higiene"). Published for the Institute of Hygiene of Santiago. Director, Dr. F. PUGA BORNE. Tome II., October, 1895., No. 5. Santiago de Chile : Cervantes.

IN attention paid to public health, as well as in other matters not a few, Chile is strikingly in advance of the other South American republics.

The present number contains an investigation of Eberth's bacillus in a dejection by a typhoid patient.

Then follows an account of the epidemic of typhoid fever in the hills Alegre and Concepcion and the Water of Quebrada Verde—a report presented to the magistracy of Valparaiso by L. E. Mourgues, M.D. (Paris).

The author found the water of the reservoir of San Agustin in a deplorable state. Nitrates and nitrites were both determined, as also free and albumenoid ammonia The water was much contaminated with organic matters

of animal and vegetable origin, and the quantity of chlorine corroborated this conclusion. The micro-organisms found were *B. coli communis* and *B. typhi abdominalis.* Dr. Mourgues recommends filtration.

Another paper treats of pepper and its falsifications in Chile, and is illustrated with cuts of the chief adulterants, such as white and black mustard, linseed, shells of olives, nuts, almonds, and hemp seed, the fruit of buckthorn (*Rhamnus cathartica*), &c.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 1, July 6, 1896.

The Perpetual Secretary announces that the Institute being in definitive possession of the funds of the bequest of Jean Jacques Berger, the various Academies will be able, setting out from 1897, to award the Jean Jacques Berger prize to the most meritorious work concerning the city of Paris. For a first period of five years the prize awarded by each of the five Academies will be of the value of 12,000 francs. After the year 1909 the value of the annual prize will be raised to 15,000 francs. In 1899 the prize will be awarded by the Academy of Sciences.

The Academy proceeded to nominate a correspondent for the Section of Astronomy, *vice* Hind, deceased. Mr. Christie obtained the votes of all the members present and was proclaimed elected.

**Researches on Tungsten.**—Henri Moissan.—Will be inserted in full.

**Solubility of Carbon in Rhodium, Iridium, and Palladium.**—Henri Moissan.—Rhodium, palladium, and iridium, like platinum, readily dissolve carbon at the temperature of the electric furnace, abandon it in the form of graphite prior to solidification, and do not form carbides. All these graphites are capable of sprouting.

**Opening a " Pli Cacheté."**—M. Loiseau demanded the opening of a " pli cacheté " which he had deposited on March 6th, 1888. It bears the title " Note on certain Properties of Raffinose serving as the Basis of a Method for the Determination of that substance, of Dextrine, and of Saccharine in Sugary Products."

**Refraction and Diffraction of the X Rays.**—M. Gouy. —It is established with certainty that if diffraction exists as it does for light the wave-length of the X rays is considerably smaller than $0.005\,\mu$, which represents $\frac{1}{100}$th of the wave-length of the green. Nothing indicates that there exists any diffraction whatever.

**Action of Zinc upon a Photographic Plate.**—R. Colson.—I have observed that zinc exerts upon platinobromide an energetic action. If we clean with sand-paper a portion of leaf-zinc which has been left to itself for some time, and bring it into contact with a gelatino-bromide plate for about 24 hours, development causes a deep grey tint to appear opposite the cleaned part and of a lighter grey opposite the parts still bright though not recently cleansed, whilst scarcely anything appears opposite the oxidised parts. This action appears also at a distance and through certain bodies. The cause seems to be vapour of zinc. Magnesium and cadmium give the same effect, but nothing is obtained with lead, tin, copper, iron, and aluminium.

**Action of Nitrogen Peroxide upon Antimony Tetrachloride.**—V. Thomas.—Nitrogen peroxide does not combine with antimonious chloride. Antimony bromide, near its melting-point, gives rise to an escape of bromine if submitted to the action of nitrogen peroxide whilst the gas is absorbed.

**Action of High Temperatures on certain Sulphides.** —A. Mourlot.—By means of the electric furnace we have obtained the crystallisation of the lead, antimony, zinc, and cadmium sulphides. The two first mentioned are decomposed into pure metal without the formation of sub-sulphides.

**On Two Isomers of Anethol.**—Charles Moureu.— Ortho-anethol and meta-anethol, which form the subject of this paper, have not yet occurred in nature. Paranethol exists in abundance, and forms at least 19·20ths of the essence of aniseed met with in commerce.

**Action of Ethyloxalyl on Naphthalene in presence of Aluminium Chloride.**—L. Rousset.—The method with aluminium chloride has been, at the suggestion of M. Bouveault, applied to the naphthalene series with success. The author describes the products obtained.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 1.

**Reactions of the Pigment of Bacillus prodigiosus.** — Bordoni Uffreduzzi. — The colour reactions of this bacillus agree partially with those of magenta. But the bacillus colour is brightened by mineral acids, is not changed by alkalis, and can be fixed upon wool in an alkaline solution.

**Analysis of Yeast.** — P. Guishard (*Bull. de la Soc. Chim.*

**Vegetable and Animal Oils in Mineral Oils.**—W. de la Royère (*Revue des Falsifications*).—The author employs the property of very dilute solutions of rosaniline to form colouring matters with acids.

**Determination of Sulphur in Pyrites.**—(See CHEMICAL NEWS: T. S. Gladding, lxx., p. 181; G. Lunge, lxxi., p. 132; Frank Johnson, lxx., p. 212).

**Determination of Sulphur in Roasted Copper Ores and Cupriferous Pyrites.**—Keller and Maas (*Journal of the Franklin Institute*).

**Valuation of Wool-Fat.**—F. v. Cochenhausen (*Dingl. Pol. Journ.*).

**Approximate Valuation of Crude Cresol.** — A. Schneider (*Pharm. Central Halle*).

**Volumetric Determination of Formaldehyd.**—M. Klar (*Pharm. Zeit.*) has improved the operation by using as indicator congo-red.

**Alkaloidal Reactions of Acetanilide.** — E. Schär (*Archiv der Pharm.*).

**Atomic Weight of Molybdenum.**—Karl Seubert and W. Pollard (*Zeit. Anorg. Chemie*).—The mean value for molybdenum is 95·772, or, if reduced to a vacuum, 95·735.

**Re-determination of the Atomic Weight of Yttrium.** —Harry Jones.—If $O = 16$ and $S = 32$ the author deduces from his determinations the mean value for yttrium as 88·95.

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# THE CHEMICAL NEWS.

VOL. LXXIV., No. 1915.

## AN AUTO-PNEUMATIC STIRRER.

### By H. BREARLEY.

IN the laboratory of large steel works, carbon by combustion is an every-day requirement; it is, indeed, no uncommon thing to find one or two assistants engaged solely on this work, making from five to ten estimations per day. The most tedious part of the determination is the decomposition of the steel and the subsequent solution of the deposited copper. This is particularly true of low carbon steels and bar irons which bore lumpy.

The common practice, after adding the copper ammon. (potass. or sodic) chloride, is to use a glass rod for bringing fresh portions of the solution into contact with the metal, or, in better appointed laboratories, to use a mechanical stirrer, such as Taylor's "duplex circular" or the one described by Blair ("Chem. Anal. Iron," p. 139, 2nd edit.). Exposed to the fumes the metal parts of these become foul; they are rather expensive, take up considerable room, and sometimes throw out the solution.

The illustration itself almost explains the new form of stirrer. The centre bottle is exhausted through the elongated funnel by attaching to a Bunsen filter-pump, or simply an ordinary filter-tube. The borings and acidified copper solution (as recommended by Langley, CHEMICAL NEWS, lxix., 4) having been placed in the flask, the first one is attached to the "exhaust" bottle, the second one to the first, third to second, and so on according to the power of the pump.* The last one is attached to a wash bottle containing lead acetate solution, so as to free the air from carbonaceous grit and sulphuretted hydrogen. When the filter-pump is started the centre bottle is exhausted, and there is a continual passage of air through the whole series, to fill up the partial vacuum. This keeps the solution in constant motion, always bringing fresh portions into contact with the metal.

Two or more series may be run by fitting an additional tube into the exhaust bottle and regulating the pressure by clips, and the solution may be effected in beakers by fitting a bell-jar with smeared edges on to a ground-glass plate, placing the beaker thereunder, and passing the tubes through the stopper. But for most purposes flasks are preferable. I know of none so satisfactory for this and many other purposes as the "Registered Pattern Flask." The sole maker is Mr. J. Preston, Fargate, Sheffield. I am not aware that it has ever been previously described. It was designed by the present Principal of the New South Wales Metallurgical Deparment—James Taylor, B.Sc.—about thirteen years ago. It combines the advantages of the conical and globular flask,—that is, every part can be readily reached by a "policeman," and a small quantity of liquid for boiling covers the bottom. In this case it is especially useful, because, having a small base, the borings lie near the in-rushing bubbles and are the more thoroughly mixed with the solution.

It is important to note that there is no grinding of the carbonaceous residue. It largely retains the shape of the boring, and is so easily washed from the flask with a jet of water that a sample may be filtered and washed free from chlorides in fifteen minutes. We use a smooth funnel, with a ¾-inch perforated platinum† plate in the throat and covered with asbestos.

As generally dissolved, the carbonaceous residue in chromium and tungsten and much-worked steels has a very irritating tendency to run through the filter. Since March, 1895, amongst a great number of such steels there has been no trouble whatever, except in a solitary case, where we had to make a more compact filter than usual and wash with alcohol. With ordinary steels the residue is very coarse, and an open filter may safely be used. When the only sample of steel available has been too small to be bored—small screws, and the like—the residue has been perfect in form, even to the threads.

Eight or ten years ago we used a similar arrangement for recovering copper from residues. For two years it has been used for the purpose named, and personal experience —reaching to nearly a thousand estimations—has proved it to be satisfactory.

To sum up its advantages:—It is cheap, requires no power every laboratory is not equipped with, takes up no additional room, has no parts to be acted on by fumes, breaks no glass ware, facilitates subsequent operations, and effects the solution cleanly, effectively, and quickly.

We find it convenient to start the samples just before leaving the laboratory. A very gentle air-current dissolves them before morning.
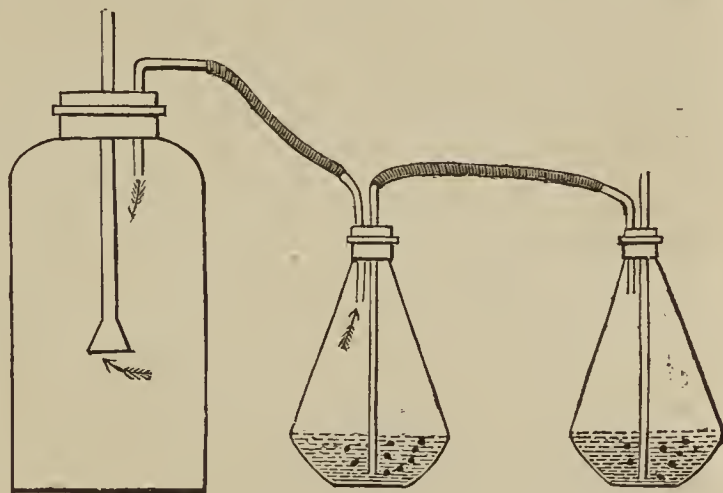


Occasionally a carbon estimation by combustion is required very quickly in a sample of steel to which the colour method cannot be applied. In such cases the following procedure has been found very convenient:— Place sample and solution into flask as usual, and close the mouth with a solid stopper. Whirl the solution round and round by moving the flask in a small circle, now one way and now the other. In a few minutes, depending on the kind of borings and the percentage of carbon, the precipitated copper will have all dissolved, except a particle here and there. Wash the stopper, allow to settle five minutes or so, and filter, &c.

The annexed examples will give some idea of the rapidity with which samples may be prepared for combustion. Five grms. of steel were taken and between 350 and 400 c.c. of copper ammon. chloride — saturated solution.

| Per cent C. | Time to dissolve. | To filter, wash Cl free, and boat. | Total. |
|---|---|---|---|
| I. 0·36 | 15 minutes. | 15 minutes. | 30 minutes. |
| II. 0·74 | 5 ,, | 15 ,, | 30 ,, |
| III.* 0·72 | 4 ,, | 7 ,, | 16 ,, |

\* Tungsten was present.

I. and II. were filtered immediately. About half-way through the filter choked somewhat, and the solution ran through in drops rather than a continuous stream. It is an advantage, from a speed point of view, to let the carbonaceous residue settle a few minutes (e.g., III. settled five minutes). An estimation may be made in from 1 to 1½ hours if the moist combustion process is used.

The Laboratory, Norfolk Works, Sheffield.

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\* We have a simple tube and 12 feet fall of water. A series of twenty is very readily agitated.

† Copper discs may be used, but they do not last long.

## COMMERCIAL PREPARATION OF BORON,

## THE ELECTRO CATALYTIC ACTION OF THE ELEMENT.

By H. N. WARREN, Principal Boron Carbon Battery Co.

THE element boron, which up to the present date has ranked mainly as a chemical curio, chiefly on account of its costliness, has now shared a fate similar to so many of the hitherto scarcer elementary bodies which advanced science has thought fit to enrol under the title of ordinary.

An improved method for the preparation of this substance, which is now made in large quantity by the above Company (and which is entirely consumed in the preparation of boronised graphite used in the construction of their primary batteries) is brought about as follows :—

Boracic acid, after calcination, in order to deprive it of its water of crystallisation, and thus convert it into boron trioxide, is ground to a fine powder, and intimately mixed with a suitable proportion of magnesium sodium chloride; the mixture is now rapidly heated to fusion, and metallic sodium introduced from time to time in large pieces, and the mass well stirred after the introduction of each piece. The reaction thus afforded is extremely moderate, but intense heat is evolved; metallic magnesium in the first instance being set free, in accordance with the following equation :— $MgCl_2 + 2Na = 2NaCl + Mg$, which at once attacks the boron trioxide, forming MgO, and free boron, $3Mg + B_2O_3 = 3MgO + 2B$. The pasty mass thus formed is detached from the crucible and thrown into an excess of HCl, when all dissolves out save the boron, which is filtered, washed, and dried. After further heating in special atmospheres, the boron is procured peculiarly active; when impregnated with graphite resembling, to a certain extent, the surface action of platinum-black.

Carbons thus prepared, about 5 inches by 2, when arranged as an outer or positive element of a battery, and charged with chromic acid solution, have been found sufficiently effective to evolve over 5 ampères from each carbon. Small cells thus arranged, equal in size to a quart Bunsen cell, give over 240 amp.-hrs., or 25 ampères for twelve hours constant.

The general and most favourable depolarisers employed with these carbons is either a saturated solution of ferric chloride and oxide of manganese, which at the same time furnishes a recuperative solution, or, secondly, chromic acid, or the still more energetic action afforded by potassium permanganate when duly acidulated.

So great has been the demand for these primaries as a motive power, where great potential is required, together with quantity, that nearly a quarter of a million of carbons so prepared have been manufactured by the Company during this season, consuming several pounds of boron per week.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

## OCCURRENCE OF AMMONIACAL NITROGEN IN PRIMITIVE ROCKS.

By HUGO ERDMANN,

DURING researches on argon and helium with which I have been engaged for some time, in concert with Prof. Dr. E. Dorn, the Director of the Physical Institute of Halle, it occurred to us that a series of minerals from Finland and Scandinavia displayed very distinctly, along with more or less helium, the bands of nitrogen when we heated the pulverised mineral in a vacuum in admixture with potassium dichromate, and examined in a Plücker tube the gas evolved. As quite especial attention had been given to the absolutely tight fitting of our apparatus, the quantities of nitrogen observed could not be derived from the atmosphere.

This phenomenon was especially striking in two newly-discovered minerals from Finland, the one closely allied to polykrase and the other very similar to euxenite. Whilst the latter mineral on spectroscopic examination displayed, along with the yellow and green helium lines, the lines of nitrogen only with moderate brightness, the Finnish polykrase, which contains no helium, evolved so bright and clear a spectrum of nitrogen that this mineral evidently contains nitrogen in a ponderable amount, and, as experiments showed, in the state of ammonia.

On a further examination it appeared that the occurrence of ammoniacal nitrogen in the northern primitive rocks is a very general phenomenon. From L. Schmelak, of Christiania, I have received a collection of beautifully crystalline Scandinavian minerals, containing some earths accompanied by more or less helium, but almost invariably nitrogen.

As instances he gives columbite, containing N, 0·067 per cent; yttrotitanite, with N, 0·0018; orthite, with N, 0·014.

Ammoniacal nitrogen has hitherto been rarely found in minerals. Its most common mineral source is carnallite. In this mineral the source of the carnallite is a maritime fauna which has perished. It is quite different with the ammoniacal nitrogen of the northern primitive rocks, which, according to the formation and deposition of such rocks, must be regarded as primitive nitrogen. This nitrogen will have been of the greatest importance for the origin of the vegetable world. At present almost the entire flora nourishes itself from animal nitrogen, which in a combined state goes through the well-known circulatory process. But how did the plant obtain combined nitrogen before there existed an animal world rich in nitrogen? The remarkable symbioses which enable the leguminoses to assimilate atmospheric nitrogen are evidently complicated phenomena of adaptation which cannot extend back to the origins of the vegetable world. For these commencements of plant-life it cannot have been indifferent that there were minerals—especially abundant in the North—where the atmospheric conditions were first suitable for the growth of plants; minerals which readily split off ammoniacal nitrogen under the influence of the atmosphere. At present agriculturists would do well to remember that there exists mineral nitrogen which, as the primitive stones weather, can be at once assimilated by all plants.—*Berichte*, xxix., p. 1710.

## RAPID DETERMINATION OF CARBONIC ACID IN THE AIR AND IN CONFINED PLACES.

By M. HENRIET.

WE search for carbonic acid in the air and in confined localities by means of an arrangement which allows of a very rapid and very accurate determination. The reaction upon which we depend is the sollowing :—

On adding sulphuric acid to a solution of neutral potassium carbonate, coloured red by means of a drop of phenolphthalein, the colouration disappears at the moment when half the carbonic acid of the carbonate is fixed upon the undecomposed carbonate, converting it into bicarbonate. This decolouration is very sharp if we take care, towards the end of the operation, to add the acid only drop by drop.

If we absorb in potassa the carbonic acid contained in a known volume of air, it is sufficient to titrate an equal

volume of the potassa liquid employed, when the difference of the readings multiplied by 2 corresponds exactly to the carbonic acid retained. We see that the result is independent of the carbonate which potassa liquid always contains, since in the liquid and in the carbonated liquid the pre-existing carbonate is decomposed by the same acid volume, and we take account merely of the difference of the readings.

Three experiments on artificial atmospheres of about 6 litres each gave the following figures:—

| $CO_2$ introduced. C.c. | Found. C.c. | Difference in fraction of volume. |
|---|---|---|
| 2·400 | 2·430 | $\frac{1}{80}$ |
| 4·431 | 4·407 | $\frac{1}{185}$ |
| 5·596 | 5·594 | $\frac{1}{2800}$ |

If we refer the gaseous volume to 100 cubic metres of air, we see that the error is—

| For 40 litres $CO_2$ | .. | 0·5 litre. |
|---|---|---|
| ,, 74 ,, | .. | 0·4 ,, |
| ,, 92 ,, | .. | 0·0 ,, |

It seems independent of the gaseous volume, and corresponds, in reading off the liquid poured out, to half a drop of the titrated liquid.

The specimen is taken in a flask of refractory glass containing about 6 litres, closed with a stopper of caoutchouc traversed by a bromine tube, penetrating into the neck of the flask by a few centimetres only, and by a second tube bent at right angles and fitted with a cock.

To take a sample of air we make a vacuum in the flask by means of a pump. We may further fill the flask with water, and empty it at the moment of taking the sample; but in this case it is proper, after having allowed the water to run away, to wash the flask with distilled water, and cause it to drain as completely as possible.

Whatever is the means adopted, when the flask has been stoppered we wait until the temperature within and without are in equilibrium. At this moment we close the cock of the elbow-tube and note the temperature.

When the flask is brought back to the laboratory we introduce into the bromine-tube 2 c.c. of ether and 15 c.c. of a pure solution of potassa (8 grms. per litre), the supernatant ether protecting the potassa against the carbonic acid of the external air. Whilst the flask cools in a current of water we introduce the potassa up to the stratum of ether. We repeatedly wash the bromine-tube with boiled water free from carbonic acid, introducing each time water into the flask. When the liquid, coloured more and more feebly by the phenolphthalein, becomes absolutely colourless, we agitate the liquid of the flask, giving it an oscillatory motion, which enables us to wet the sides of the neck. We let the contact continue for an hour, agitating at several intervals. The absorption is then complete.

We open the cock of the elbow-tube. The air escapes under a slight pressure. We then add the standard acid (1 c.c. of which is equivalent to 0·5 c.c. of carbonic acid) until the decolouration is complete, without fearing the influence of the carbonic acid of the external air, because the flask is full of decarbonated air.—*Comptes Rendus,* cxxiii., second half-year, p. 125.

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## AN IODOMETRIC METHOD FOR THE DETERMINATION OF CARBON DIOXIDE.*

### By I. K. PHELPS.

IN a recent paper from this laboratory (*Am. Journ. Sci.,* l., 101), it has been shown that carbon dioxide may be

estimated with accuracy by absorbing it under prescribed conditions in barium hydroxide, washing away the excess of the hydroxide, and converting the precipitated carbonate to the form of the sulphate. The chief difficulty in the process was occasioned by the fact that the barium carbonate precipitated from cold solutions is so finely divided and non-crystalline in character, that the removal of the excess of the hydroxide by filtration is a somewhat delicate and tedious process. The possibility of taking up by iodine the excess of the hydroxide remaining after the precipitation of the carbonate, and then determining the excess of iodine volumetrically, furnished the incentive to the following experiments.

The process, as finally developed, consists of three steps :—First, the evolution of the carbon dioxide and its collection in barium hydroxide contained in a partially evacuated flask: secondly, the conversion of the excess of the hydroxide to the form of iodide and iodate by adding an excess of iodine; and, thirdly, the titration of the excess of iodine with standard arsenious acid.

The barium hydroxide solution was prepared for use by filtering a cold saturated solution into a large bottle, from which it was drawn, or pumped, by means of the little improvised pump described by Kreider (*Am. Journ. Sci.,* l., 132); in either event care was taken to feed the air, which took the place in the bottle of the hydroxide removed, through potash bulbs to prevent the introduction of atmospheric carbon dioxide. The solution of barium hydroxide was standardised by drawing 80—90 c.m.³ of decinormal iodine into a glass flask, provided with a ground-glass stopper carrying an inlet tube reaching nearly to the bottom of the flask, and an outlet tube to which was sealed a Will and Varrentrapp absorption apparatus, and then introducing an appropriate amount of the barium hydroxide solution either from a burette or from a stoppered funnel which was weighed before and after. An ether wash-bottle answers admirably for a standardising flask, and with the glass stopper and its attachments replaced by a rubber stopper, answers the purpose of the absorption flask described later. The glass stopper is introduced, the inlet being closed by a rubber cap, and the absorption apparatus is charged with a solution of potassium iodide, to hinder the escape of iodine. The solution was brought to a boil, then cooled, and the excess of iodine determined by decinormal arsenious acid. It is assumed that the iodine lost acted on barium hydroxide according to the equation—

$$6BaO_2H_2 + 6I_2 = Ba(IO_3)_2 + 5BaI_2 + 6H_2O.$$
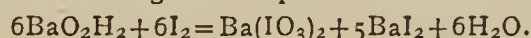
It was found necessary to boil the solution because of the formation of traces of the hypoiodite, which is broken up into iodide and iodate only by boiling, but which, if left unchanged, acts subsequently on the arsenious acid used in titrating the free iodine.

The apparatus which I have found most convenient for evolving the carbon dioxide from the carbonate consisted of a wide-mouthed flask of about 75 c.m.³ capacity, furnished with a doubly perforated stopper carrying a separating funnel for the introduction of acid into the flask, and a tube of 0·7 c.m. internal diameter, which is expanded to a small bulb just above the stopper, to carry off the gas. This exit tube was joined by a rubber connector to a tube which passed through the rubber stopper, closing the absorption flask (the ether wash-bottle used in standardising the barium hydroxide solution described above), and which ended in a valve preferably of the Kreider pattern (*loc. cit.*). This valve was enclosed in a larger tube reaching nearly to the bottom of the absorption flask. Through a second hole in the stopper of the absorption flask passed a glass tube closed by a rubber connector and screw pinch-cock.

In making a determination of carbon dioxide, the carbonate was introduced in weighed portions into the boiling flask. Barium hydroxide solution, in amount from 7—10 c.m.³ more than actually necessary to precipitate the carbon dioxide, was drawn into the absorption flask, which was

then connected with the boiling flask, as described above. The stopcock of the separating funnel was shut off, and the flasks evacuated by connecting the exit tube of the absorption flask with a filter flask previously pumped out by the water pump, a mercury manometer registering the pressure. Exhaustion to a pressure of from 250—300 m.m. was found sufficient and easily attainable with the available water pressure in a minute's time. Sufficient phosphoric acid (chosen as a non-volatile acid) to dissolve the carbonate was introduced into the stoppered funnel with about 50 c.m.³ of water, which had been previously purified from carbon dioxide by boiling until one-third had been driven off in steam, and kept in full, stoppered flasks until used. The acid was then allowed to enter the boiling flask, and the carbon dioxide driven over completely to the absorption flask by boiling for five minutes —the latter being shaken frequently during the passage of the gas into it, and kept cool by standing in a dish of water. The atmospheric pressure was then restored by admitting purified air through the funnel of the boiling flask. In the experiments of Table I., the inlet tube of the absorption flask was closed by a rubber cap after disconnection, the exit tube was attached to potash bulbs, and the flask was cooled in a stream of water. The exit tube was removed, a capillary tube long enough to reach below the surface of the liquid introduced, and decinormal iodine run in until the large excess of barium hydroxide had been destroyed. Then the glass stopper of the absorption flask was introduced, with a rubber cap on the inlet tube and potassium iodide solution in the trap, as in standardising, and the emulsion brought to a boil. Iodine was again run into the hot solution through the inlet tube until the colour remained distinctly red after a second boiling. After cooling, the excess of iodine was determined by standard arsenious acid.

TABLE I.

| CaCO₃ taken. Grm. | BaO₂H₂ taken. Grms. | BaO₂H₂ found. Grm. | CO₂ found. Grm. | Error. on CO₂. Grm. | Error. Corrected. Grm. |
|---|---|---|---|---|---|
| 1. 0·0501 | 0·2484 | 0·1604 | 0·0227 | 0·0006 + | 0·0007 + |
| 2. 0·0500 | 0·2381 | 0·1508 | 0·0224 | 0·0004 + | 0·0005 + |
| 3. 0·1022 | 0·3416 | 0·1675 | 0·0447 | 0·0003 − | 0·0001 − |
| 4. 0·1026 | 0·3105 | 0· 351 | 0·0450 | 0·0001 − | 0·0000 |
| 5. 0·2032 | 0·6181 | 0·2692 | 0·0896 | 0·0002 + | 0·0004 + |
| 6. 0·2049 | 0·5761 | 0·2223 | 0·0908 | 0·0006 + | 0·0008 + |
| 7. 0·5088 | 1·1301 | 0·2606 | 0·2232 | 0·0007 − | 0·0000 |
| 8. 0·5015 | 1·0804 | 0·2245 | 0·2197 | 0·0010 − | 0·0003 − |
| 9. 1·0032 | 2·0125 | 0·3004 | 0·4394 | 0·0020 − | 0·0006 − |
| 10. 1·0064 | 2·0702 | 0·3538 | 0·4405 | 0·0023 − | 0·0009 − |

In Experiments 7, 8, and 9, the barium hydroxide solution was estimated by weight—in the others by volume. The calcium carbonate used was Iceland spar in the form of chips, but, though it was the best material available and considerably better than the best commercial calcium carbonate at hand, the test of drying below red heat and the igniting to the condition of caustic lime with a blowpipe, proved it to be slightly deficient in carbon dioxide. The observed correction of 0·0014 grm. for each grm. of the carbonate is applied in the last column of the table.

The low results of the larger amounts of carbon dioxide, in contrast to the higher results of the smaller amounts, point to some action of the iodine upon the precipitated carbonate. It would be natural to suppose that such action would be greater upon the carbonate precipitated from a cold solution, and this proved to be the case. For when barium carbonate, precipitated under the conditions of the analysis described, was treated with 10 c.m.³ of iodine and boiled again, a loss of 0·0044 grm. of iodine (corresponding to 0·0008 grm. of dioxide) was found; but when barium carbonate was prepared by passing carbon dioxide through a cold solution of barium hydroxide until the presence of the acid carbonate was proved in solution by filtering a portion and boiling—thus insuring the complete destruction of the hydroxide—the precipitated carbonate, after filtering and washing, was

acted upon by 10 c.m.³ of iodine solution to such an extent that 0·0253 grm. of iodine (corresponding to 0·0044 grm. of carbon dioxide) disappeared. The obvious inference is, therefore, that the carbonate should be boiled before the addition of iodine in the process.

The experiments of Table II. were made like those of Table I., excepting in the following points :—First, an ordinary flask of about 300 c.m.³ capacity, which, fitted with a rubber stopper, was substituted for the more expensive ground stoppered absorption flask; secondly, the precipitated carbonate was boiled before adding any iodine; and thirdly, after iodine was added to a yellow colour and boiled, a second amount of iodine was run in to a red colour, but the mixture was not boiled again. By this treatment the iodine is kept from acting on the precipitated carbonate, at least to such an extent that the action is not appreciable, and from attacking the rubber stopper used; incidentally, it is kept from entering the trap, but one is used, nevertheless, to prevent contamination from the outside air. A separating funnel, reaching below the surface of the liquid, was found a convenient means of introducing the iodine without loss into the hot solution. A higher vacuum is required when the smaller flask is used, especially when large amounts of carbon dioxide are to be determined. A pressure of 200 m.m. of mercury was found to be sufficiently low, and in no case did a flask of ordinary thickness and of 300 c.m.³ capacity collapse at that degree of exhaustion.

TABLE II.

| CaCO₃ taken. Grm. | BaO₂H₂ taken. Grms. | BaO₂H₂ found. Grm. | CO₂ found. Grm. | Error on CO₂. Grm. | Corrected error. Grm. |
|---|---|---|---|---|---|
| 1. 0·5023 | 1·1385 | 0·2851 | 0·2190 | 0·0020 − | 0·0000 |
| 2. 0·5056 | 1·1414 | 0·2801 | 0·2211 | 0·0014 − | 0·0006 + |
| 3. 1·0011 | 2·0712 | 0·3704 | 0·4367 | 0·0038 − | 0·0002 + |
| 4. 1·0030 | 1·8788 | 0·1736 | 0·4376 | 0·0037 − | 0·0003 + |

The calcium carbonate used in this test of the smaller apparatus was the purest commercial article available ; the error applied as a correction in the last column (0·0040 grm. on carbon dioxide for a grm. of carbonate) was determined by five closely-agreeing analyses of various amounts in the larger apparatus.

The process, beside being delicate, is fairly rapid—the average time for a determination being about three-quarters of an hour.

It only remains to thank Prof. F. A. Gooch for many helpful suggestions and kindly advice in this investigation.

## THE GRAVIMETRIC DETERMINATION OF SELENIUM.*

### By A. W. PEIRCE.

THE method generally in use for the gravimetric determination of selenious acid is to precipitate the selenium with sulphurous acid in presence of hydrochloric acid and to weigh the elementary selenium. Precipitation by this method, however, is slow and incomplete in many cases, so that it is always necessary to treat the filtrate a second time with sulphurous acid and to digest for some time. To obviate the necessary delay in this process, I have tried the effect of substituting potassium iodide as the reducer instead of the sulphurous acid, adopting the idea from several recent volumetric methods for the determination of selenium† in which an iodide in acid solution is used to reduce the selenious acid, and in which the

liberated iodine, caught in various ways, is titrated and
aken as a measure of the selenium.

Varying amounts of selenium dioxide, prepared according to the method described in former articles, by dissolving pure selenium in nitric acid, removing any selenic acid formed by barium hydroxide, and subliming in a current of dry oxygen, were dissolved in Erlenmeyer flasks, and the solution was acidified with hydrochloric acid; potassium iodide was added and the selenium was precipitated in the form of a red powder. Boiling for ten minutes served to reduce most of the liberated iodine and to change the selenium into the black modification, which was collected upon an asbestos felt, washed, dried at 100° to a constant weight, and weighed. Early experiments showed that for small amounts the process gave accurate results, but that for large amounts the errors came far too high :—

| Se taken. Grm. | Se found. Grm. | KI. Grms. | Volume. C.m.³. | Error. Grm. |
|---|---|---|---|---|
| 1. 0·0355 | 0·0356 | 1 | 100 | 0·0001+ |
| 2. 0·0355 | 0·0355 | 1 | 100 | 0·0000 |
| 3. 0·0355 | 0·0356 | 1 | 100 | 0·0001+ |
| 4. 0·2968 | 0·3883 | 4 | 75 | 0·0915+ |
| 5. 0·2033 | 0·2475 | 4 | 100 | 0·0442+ |
| 6. 0·3058 | 0·3495 | 10 | 100 | 0·0437+ |

When the selenium amounted to less than a tenth of a grm. the results came out well. When the amount was larger the selenium assumed on boiling a pasty molten condition, which made filtering and washing impossible. This condition was observed in the work already referred to, and the mass seemed to consist of selenium with included iodine, as it gave up iodine slowly to water on standing, and more rapidly to a solution of potassium iodide.

It has been found in the work to be described that if an excess of potassium iodide be used considerably above the amount necessary for precipitation, the pasty condition of the selenium does not occur, the iodine evidently being held in solution by the excess of the potassium iodide. This would seem to indicate the total release of the iodine, and would make possible the determination of quantities larger than the two-tenths of a grm. set in the former work as a limit for the range of the process. Several determinations, which resulted very satisfactorily, were made according to the volumetric method thus modified, and at the same time the selenium which was precipitated was weighed. By the former method, in which the iodine evolved was estimated, the results were too low; and by the latter method, in which the residue was weighed, too high; but there appeared to be no definite relation between the errors of the two processes, as there would be if the retention of iodine were the only difficulty. Digestion of the selenium in the crucible with hot water removed a small amount of potassium iodide and reduced the error considerably; so that it was apparent that the increase in weight was due to the fact that the precipitated selenium included potassium iodide from the concentrated solution.

| SeO₂ taken. Grm. | SeO₂ found. Grm. | KI. Grm. | Vol. Cm³. | Error. Grm. | Se taken as SeO₂. Grm. | Se found. Grm. | Error. Grm. |
|---|---|---|---|---|---|---|---|
| 7. 0·4870 | 0·4868 | 7 | 60 | 0·0002− | 0·3467 | 0·3507 | 0·0040+ |
| 8. 0·4980 | 0·4971 | 10 | 60 | 0·0009− | 0·3545 | 0·3575 | 0·0030+ |
| 9. 0·7323 | 0·7310 | 10 | 75 | 0·0013− | 0·5214 | 0·5312 | 0·0098+ |

Later experiments under similar conditions, excepting that the volume of the liquid in which the precipitation took place was very much increased, so that the tendency on the part of the selenium to include the iodide might be diminished, gave errors entirely within satisfactory limits, though always positive. (See Table, next col.).

It is sufficient to dilute to 400 c.m.³ before acidifying with hydrochloric acid and adding potassium iodide to an amount about 3 grms. in excess of that actually required. Boiling for ten to twenty minutes will change the selenium

| Se taken as SeO₂. Grm. | Se found. Grm. | KI. Grms. | Volume. C.m.³. | Error. Grm. |
|---|---|---|---|---|
| 10. 0·2853 | 0·2861 | 7 | 900 | 0·0008+ |
| 11. 0·3189 | 0·3192 | 8 | 400 | 0·0003+ |
| 12. 0·3318 | 0·3324 | 7 | 500 | 0·0006+ |
| 13. 0·3798 | 0·3805 | 7 | 500 | 0·0007+ |
| 14. 0·4252 | 0·4259 | 7 | 350 | 0·0007+ |
| 15. 0·4430 | 0·4434 | 10 | 450 | 0·0004+ |

to the black modification and remove most of the iodine. The process of precipitation and filtering can be completed in half an hour. The selenium is dried at 100° to a constant weight.

When the selenium occurs in the higher form of oxidation the reduction follows the same course, though iodine is not liberated until the solution is quite warm; but at the end of the usual time of boiling the action is complete. The following shows the results obtained by acting in the manner described on selenic acid.

| SeO₃ taken. Grm. | Se taken. Grm. | Se found. Grm. | KI. Grms. | Volume. C.m.³. | Error. Grm. |
|---|---|---|---|---|---|
| 0·1709 | 0·1063 | 0·1065 | 5 | 500 | 0·0002+ |
| 0·1709 | 0·1063 | 0·1062 | 5 | 375 | 0·0001− |
| 0·3231 | 0·2010 | 0·2017 | 5 | 350 | 0·0007+ |
| 0·5005 | 0·3115 | 0·3126 | 6 | 500 | 0·0011+ |

Evidently this method will not distinguish between selenious and selenic acids, but it will be found of much value in point of time saved in the determination of either separately, or of the total selenium in case both occur together.

The kindly advice and suggestions of Prof. F. A. Gooch are gratefully acknowledged.

# THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.*

By HENRY FAY.

*Determination of Uranium in the Brown Precipitate.*

SOME of the freshly prepared substance was partially dried between filter-papers, transferred to a porcelain boat, and then dried at 100° in a stream of dry hydrogen. The substance, prepared in this way, has a pale, greyish green colour, resembling somewhat uranous oxalate, and in this condition shows very little tendency to pass over into the yellow substance. It was weighed rapidly, placed in a combustion-tube, and heated in a current of oxygen. When heated under these conditions the substance begins to glow, and the combustion spreads rapidly throughout the mass. After a very few minutes the substance is changed into the oxide $U_3O_8$. The boat is then withdrawn and weighed. The oxide obtained in this way is of a pale olive-green colour, and appears to be perfectly pure. The uranium was determined in six separate specimens in this way :—

I. 0·4768 grm. gave 0·4407 grm. $U_3O_8$=78·47 p. c. U.
II. 0·2373　　 ,, 　0·2180　 ,, 　=77·99　 ,,
III. 0·1372　　 ,, 　0·1249　 ,, 　=78·00　 ,,
IV. 0·1556　　 ,, 　0·1414　 ,, 　=77·15　 ,,
V. 0·1856　　 ,, 　0·1699　 ,, 　=77·58　 ,,
VI. 0·1454　　 ,, 　0·1314　 ,, 　=77·41　 ,,
Average for the six determinations, 77·76 per cent U.

These results, it will be seen, are fairly concordant, but good results could not be obtained for carbon.

Several attempts were made to determine the percentage of carbon, but, on account of the relatively small amount present, the results were not satisfactory. The substance, when heated alone, gives off small amounts of carbon monoxide, but, even by passing the gases over ignited copper oxide, good results were not obtained. The yellow substance, into which the brown one passes on standing, gave better results. These will be spoken of later. Various attempts were made to isolate the acid contained in this salt, but without success. The substance dissolves readily in hydrochloric, sulphuric, and nitric acids, forming green solutions, from which ammonia precipitates the black uranous hydroxide. All that can be said at present in regard to this salt is that it is a reduction product of uranyl oxalate. There can be no doubt that it contains a small percentage of carbon, as will be made more evident when the yellow transformation-product is considered. Ebelman believed it to be a hydrated oxide, but the presence of carbon proves this assumption to be wrong. Bolton obtained the same precipitate by exposing a solution of the double oxyfluoride of uranium and potassium acidified with oxalic acid. He however did not analyse the product. If this were the simple hydrated oxide, it seems that it should also be formed with other acids than oxalic acid, especially when the same salt of Bolton is acidified with formic acid. In this case only the salt $4UF+KF$ is formed.

### Analysis of the Yellow Substance obtained from the Purplish-brown Precipitate.

The best way to prepare the yellow salt is to allow the brown substance to stand in a desiccator for four or five days. It is also formed when allowed to stand in the air, but it is more convenient to use the desiccator, as in this way the yellow salt can be obtained in dry condition having constant weight. For the analysis of this salt, it was dried to constant weight over sulphuric acid, or by heating in an air-bath to 100°. The substance is also formed when the brown precipitate is allowed to stand under water for several weeks. A preliminary test for carbon was made by heating the substance in a tube through which pure air was drawn. The gases were passed into barium hydroxide solution. There was considerable barium carbonate formed, showing carbon to be present.

This substance was heated in a combustion-tube as in the previous case, and the uranium oxide afterward weighed, the uranium, carbon, and hydrogen being thus estimated in the same operation. The substance was first converted into a brick-red substance, probably $U_2O_5$, and on higher heating gave the oxide $U_3O_8$.

Different preparations gave the following results on analysis :—

|      | U.              | C.              | H₂O.            |
|------|-----------------|-----------------|-----------------|
| I.   | 75·46 per cent. | 1·36 per cent.  | 8·58 per cent·  |
| II.  | 75·40  „        | 1·02  „         | 8·04  „         |
| III. | 75·10  „        | 1·2  „          | 8·50  „         |
| IV.  | 74·9  „         | 1·15  „         | 8·7  „          |
| V.   | 75·44  „        | —               | —               |

These results are selected from a much larger number of analyses, all of which agree very closely with the ones given.

It is difficult to account for the small amount of carbon present, but as none of the carbon was given off in the original decomposition, and the brown substance does not lose any carbon dioxide in drying, it is safe to say that all of the carbon is in combination with the uranium. In what form it exists is impossible to say, as the substance dissolves in acid without separation of any organic acid. If all the uranium is precipitated and the filtrate separated, there is no evidence of any organic substance remaining behind.

### Formation of Formic Acid in the Decomposition of Oxalic Acid.

Jones showed that the equation of Seekamp, representing the decomposition of oxalic acid by uranyl oxalate, does not express the reaction, as it does not account for the formic acid nor for the carbon monoxide. It was thought advisable to make a few experiments to see whether formic acid can be built up from carbon monoxide and water in presence of uranium salts. For this purpose the following experiments were made :—

I. A 250 c.c. Erlenmeyer flask was filled with a solution of uranyl oxalate, and about 100 c.c. carbon monoxide introduced into it. The inverted flask was connected with a long tube bent twice at right angles to show the pressure. The flask was exposed to the direct sunlight. Within two hours the decomposition of the uranyl oxalate was complete. The precipitate was the same as the one spoken of above when uranyl oxalate decomposes. No free acid was detected in the solution.

II. Carbon monoxide and water were exposed for fifteen days in the direct sunlight. On examination, at the end of this time, the water was perfectly neutral.

III. Mixtures of equal values of carbon monoxide and carbon dioxide, in the presence of water, were exposed to the direct sunlight, but no formic acid was obtained.

From these experiments it is shown that the formic acid obtained in the decomposition of oxalic acid is from the oxalic acid itself, and not from the combination of carbon monoxide and water.

### Decomposition of Malonic Acid.

The study of malonic acid was next taken up, and it was my purpose to proceed as in the case of oxalic acid, but unexpected difficulties arose.

Uranyl malonate was prepared by bringing together hot concentrated solutions of malonic acid and uranyl nitrate. It separates in a few moments as a bright yellow crystalline powder, adhering firmly to the sides of the beaker. It is nearly insoluble in water and alcohol, more readily soluble in nitric acid, and easily soluble in a solution of malonic acid.

On analysis it gave the following results for uranium :—

Calculated for $CH_2 <^{COO}_{COO}> (UO_2).3H_2O$, 56·06 p. c.

0·2526 grm. gave 0·1656 grm. $U_3O_8 = 55·65$ per cent U.
0·3682  „        0·2416  „        $= 55·70$  „  U.

Heated to 110° for four hours it lost 9·15 per cent $H_2O$.
Calculated for $2H_2O$, 8·78.

At 180°, 0·2670 grm. lost in weight 0·0325 grm. $= 12·16$ per cent $H_2O$.
Calculated for $3H_2O$, 12·6 per cent $H_2O$.

This, like many uranium salts, loses some water readily, but loses the last molecule only at high temperatures.

As this salt is almost insoluble in water, it could not be used in this work. Accordingly, dilute solutions of uranyl nitrate and malonic acid were exposed to the light, but within a few minutes the uranyl malonate was completely precipitated. The uranyl malonate dissolves in potassium malonate, and it was hoped to use such a solution for the decomposition. The double salt of potassium and uranium was made by dissolving the uranium malonate in the required amount of potassium malonate. On evaporation well-formed, but small, very bright yellow crystals were obtained. Solutions of this salt, with and without free malonic acid, were exposed to the sunlight for several days, but there was no indication of decomposition in either case. They seemed to be perfectly stable in the brightest sunlight.

The same results were obtained when the uranyl malonate was dissolved in malonic acid and the solution exposed. The malonic acid decomposes when a dilute solution of uranyl oxalate and malonic acid is exposed to the sunlight, but the rate of decomposition is so extremely slow that it was not considered advisable at the time to carry the work further.

### Decomposition of Succinic Acid.

Attempts were made to decompose succinic acid ·by means of uranyl succinate, but so far it has been impossible to effect such a decomposition.

Uranyl succinate is described in "Watts's Dictionary" as being made from uranyl nitrate and acid sodium succinate by evaporation to dryness. This method was tried, but the uranium salt obtained was so nearly insoluble in water that it was not suited for the experiments. Some of the salt obtained was dissolved in a dilute solution of succinic acid, and this solution exposed to the direct sunlight for some days showed no tendency to change. Various other methods were tried for the purpose of making uranyl succinate, but they were not successful. Solutions of uranyl nitrate and succinic acid can be evaporated to crystallisation, but they crystallise separately. It was also hoped to get it from barium succinate and uranyl sulphate. These salts were brought together in molecular proportions, but part of the barium was changed into sulphate and part into the insoluble barium uranate.

As it was desired to study the decomposition of succinic acid in the presence of uranyl succinate, the experiments were carried on further.

Seekamp (*Ann. Chem.*, Liebig, cxxxiii., 253) found that succinic acid decomposes in the sunlight, in the presence of uranyl nitrate, into carbon dioxide and propionic acid. This was verified qualitatively. The action takes place rather slowly, and, as this work could be carried on only during the winter and early spring months, it was not carried further. Seekamp believed the green precipitate in this case to be uranous succinate. A small amount of this substance was obtained and analysed for uranium, but the percentage did not agree with that required for uranous succinate.

It is necessary to do much more work on the precipitates obtained in these decompositions as they are difficult to obtain in a pure state, and, from analyses made of precipitates from other acids, they do not appear to be the simple reduction product.

### Decomposition of Tartaric Acid.

When tartaric acid and uranyl nitrate are exposed to the sunlight, the clear yellow solution gradually turns to a deep green colour, and after a few hours there is a precipitation of a light green salt. No gas is given off in the reaction. Several solutions were attached to nitrometers containing mercury, but there was no change in the volume, although the solutions were under much reduced pressure. Heat facilitates the precipitation very greatly. Some of the green solution from which the precipitate had been removed was placed on a water-bath, when there was a complete precipitation in a few minutes. The precipitate is most readily formed when 1 molecule of uranyl nitrate is exposed with 1 molecule of tartaric acid. If the solution in which the precipitate has been formed is allowed to stand in the sunlight for several weeks, the green-coloured salt passes into solution, forming an amber-coloured liquid.

For analysis the green salt was dried between filter-paper and then over solid potassium hydroxide. It gave the following results:—

I.

0·2631 grm. gave 0·1529 grm. $U_3O_8$
0·2631    „    0·0555  „   $H_2O$
0·2631    „    0·1396  „   $CO_2$.

II.

0·2949 grm. gave 0·1713 grm. $U_3O_8$
0·2949    „    0·0684  „   $H_2O$
0·2949    “    0·1662  ,,   $CO_2$.

|             | Calculated for $U_6H_{12}O_{16}$. | Found. | |
|-------------|--------------|--------|--------|
|             |              | I.     | II.    |
| Uranium .. .. | 49·58       | 49·3   | 49·31  |
| Hydrogen .. .. | 2·48        | 2·34   | 2·57   |
| Carbon  .. .. | 14·87       | 14·46  | 15·3   |

The nature of the above precipitate cannot be learned from the above results, and the formula suggested has no significance at present. It may be possible to isolate the organic portion of the salt, but until this has been done it would be useless to speculate in regard to the nature of the precipitate.

### Decomposition of Isobutyric Acid.

Wisbar (*Ann. Chem.*, Liebig, cclxii., 232) has studied the action of sunlight on butyric acid in the presence of uranium salts, and found that it is decomposed into propane and carbon dioxide. It was thought desirable to know whether the other acids of this series undergo a similar decomposition, and accordingly a study was made of isobutyric, propionic, and acetic acids. The study of isobutyric acid was taken up first, as it was found to work readily, giving off gas freely when exposed to the sunlight with uranyl nitrate.

Experiments were first made to see whether any definite relations existed between the gases given off. Carbon dioxide was shown to be present by its ready absorption by potassium hydroxide, and the residual gas was burnt from the capillary tube of the nitrometer in which it was collected. It burned with a smoky flame, showing it to be a hydrocarbon.

It was believed that the isobutyric acid would decompose in the same way as the butyric acid, giving equal volumes of propane and carbon dioxide. This was found to be the case, as is shown ·by the following experiment:—

I. For the purpose of collecting the gases the solutions were exposed in small test-tubes, 13 × 120 m.m., connected by means of a capillary tube to a nitrometer filled with mercury. The acid to be used was weighed directly into the tube, and a weighed portion of uranyl nitrate was added. Water was now added to bring the solution to the required height in the tube.

2·0201 grms. isobutyric acid and 0·3365 grm. uranyl nitrate were dissolved in 30 c.c. water and exposed to the sunlight. Gas begins to be given off about fifteen minutes after the exposure is made. After being exposed for nearly an hour the lower half of the solution becomes cloudy, and small drops of a dark green viscous liquid soon appear, which gradually collect in the bottom of the test-tube. Most of the gas evolved seems to come from this large drop. This dark green heavy liquid is, however, not always formed, and its formation depends on conditions which have not as yet been learned. A precipitate, however, is always formed—either this liquid or a light green powder.

The exposure was continued for several days when all action ceased. All of the uranium was precipitated.

The total volume of gas was 30 c.c., and of this 14·8 c.c. were absorbed by caustic potash, which shows half the volume of gas to be carbon dioxide. This also shows that the total decomposition of the acid was approximately 30 per cent of that calculated for the equation—

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\! > CH.COOH = CH_3.CH_2.CH_3 + CO_2.$$
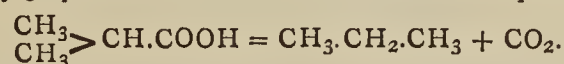
At the end of the first day's exposure 21·5 per cent of the decomposition had taken place.

II. This experiment was carried on precisely as the preceding, except that, after the reaction had begun, a tube filled with warm water was placed around the tube containing the solution. This increased the reaction very much, and it was found that by this method large quantities of the gases can be collected in a very short time. Of 27 c.c. gas collected, 13·6 c.c. were absorbed by caustic potash.

III. In this experiment much larger quantities of acid and uranyl nitrate were used for the purpose of securing a pure specimen of the hydrocarbon for analysis. After 25 c.c. of the gas had been collected, it was removed from the nitrometer, so as to get rid of any oxygen or nitrogen possibly held in solution by the water. This was repeated

several times before a sample of the gas was collected for analysis.

The gas was removed by having it under pressure by means of the pressure-tube connected with the nitrometer, and then opening the glass stopcock of the nitrometer only a little way. The stopcock was closed before all of the gas had escaped, thus making sure that no air could enter. By this means it was found possible to collect the evolved gas. On absorption, exactly half of the volume was shown to be carbon dioxide. The remaining portion was then transferred to a eudiometer and exploded with oxygen.

Volume of original gas .. .. 21·3 m.m. = 1 vol.
Volume after addition of oxygen 400·7 ,, = 18·81 vols.
Volume after explosion .. .. 335·9 ,, = 15·76 ,,
Contraction .. .. .. .. .. .. .. = 3·05 ,,

The calculated contraction for $C_3H_8$ is 3 volumes. This shows the hydrocarbon to be propane, and the reaction is to be represented by the equation—

$$C_4H_8O_2 = C_3H_8 + CO_2.$$
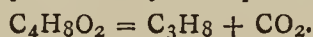
### Decomposition of Propionic Acid.

Uranyl nitrate and propionic acid, when exposed to sunlight, decompose very readily, giving off gas in a few minutes after exposure is made. It was found best to use a rather strong solution of the acid. The gas is given off evenly, and continues until nearly all of the acid is decomposed. The gas was collected and analysed in the same manner as described under isobutyric acid.

I. 32·4 c.c. of gas gave .. 15·8 c.c. $CO_2$.
II. 30·5 ,, ,, .. 15·1 ,,
III. 26·4 ,, ,, .. 13·2 ,,

These figures show that approximately half the volume of the gas is carbon dioxide.

The residual portion was run into a eudiometer and exploded with oxygen.

Volume of original gas .. .. 19·97 m.m. = 1 vol.
Volume after addition of oxygen 201·12 ,, = 10·07 vols.
Volume after explosion .. .. 147·44 ,, = 7·38 ,,
Contraction .. .. .. .. .. .. .. = 2·69 ,,
Calculated contraction for $C_2H_6$ .. .. = 2·5 ,,

This shows the hydrocarbon to be ethane, and the decomposition of propionic acid is to be represented by the equation—

$$C_2H_5.COOH = C_2H_6 + CO_2.$$
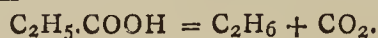
(To be continued).

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## OXIDATION OF SODIUM SULPHIDE AND HYDROSULPHIDE TO THE SULPHATE BY ELECTROLYSIS.*

### By FRANK W. DURKEE.

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IT is very well known that potassium and sodium chlorates can be made from the chlorides in solution by electrolysis, and various other substances oxidised by the same means. Sodium sulphate mixed with acid sodium hydrosulphite, $NaHS_2O_4$, has been produced from acid sodium sulphite (E. H. Ekker, *Rec. Trav. Chim.*, xiv., 57-64, 1895), but I am not aware that any one before has attempted to make sulphates from the alkaline sulphides and hydrosulphides by electrolysis. At the request of Mr. F. S. Pearson, Engineer of the Metropolitan Traction Company of New York City, experiments were begun to show whether or not it would be possible to transform the ammonium compounds in gas liquors directly into sulphate of ammonium by use of the electric current. In the preliminary experiments, gas carbon electrodes were used, and ammoniacal

sulphide and hydrosulphide solutions, but with this arrangement the three-ampère current, which passed through the solution for several hours, failed to produce any sulphate. The sulphide solution was blackened, however, by the finely divided particles of carbon which separated from the electrodes. Copper electrodes, when used in place of the carbon, were soon covered with copper sulphide, and the ammonium sulphur compounds were not oxidised. The oxidation went on very well when platinum electrodes were used, and ammonium sulphate in considerable quantity was produced. Solutions of sodium hydrosulphide and sodium sulphide were then subjected to electrolysis, and sulphate of sodium obtained. These experiments, however, were not conducted in a way to show that all of the alkaline metals in the compounds present could be changed to sulphate by electrolysis. This point seemed of so much importance that an attempt was made to settle it, first of all, at the beginning of the investigation, and in the following way :—

Fifty c.c. of a solution of sodium hydroxide, prepared from sodium and distilled water, were measured out into a small flask, and supersaturated with hydrogen sulphide. An equal volume of the same solution of sodium hydroxide was then added, and the resulting solution, approximating a sulphide, was poured into a tall beaker of about one litre capacity. 300 c.c. of water were added. To prevent loss by spattering during the process of electrolysis, the beaker was covered with a watch-glass, notched to admit the wires which extended to the electrodes. The electrodes themselves, of thick platinum foil, were cylindrical in form, three inches long and one inch in diameter. Heavy platinum wires connected the electrodes to the battery circuit. When in use, the electrodes were thrust nearly to the bottom of the beaker, were parallel, and one and a-half inches apart. After proper connections had been made with a storage battery, a current of about 3·1 ampères flowed through the liquid for about eleven hours and thirty-five minutes. Then the circuit was broken and the solid matter, mostly sulphur, filtered out. Afterwards enough water was added to the filtrate to make 1000 c.c. A second solution was then prepared in exactly the same way as the first and made up to 1000 c.c.

It followed, therefore, that 1 c.c. of the new solution contained as much sodium as 0·1 c.c. of the original solution of sodium hydroxide, and 25 c.c. as much as 2·5 c.c. of the solution of hydroxide. If, then, pains be taken to determine accurately the weight of sodium combined as sulphate in 25 c.c. of the solution after electrolysis, it should exactly equal the weight of the sodium in 2·5 c.c. of the solution of hydroxide, if the oxidation to sulphate by electrolysis is complete and quantitative. Tested qualitatively, the solutions were neutral and gave the reactions only of sodium sulphate. Consequently, to get the weight of sodium sulphate, it is only necessary to evaporate to dryness in a weighed platinum crucible, on a water-bath, 25 c.c. of the solutions after electrolysis, heat and weigh. The weight of the sodium could then be calculated from the weight of sodium sulphate found. Duplicate determinations of sodium sulphate were made in each solution, and the results are below.

### Solution No. I.

a. Weight of $Na_2SO_4$ in 25 c.c., 0·2641 grm.
b. Weight of $Na_2SO_4$ in 25 c.c., 0·2653 grm.

Weight of Na calculated from an average of weights of $Na_2SO_4$ obtained in the above determination, 0·0857 grm.

### Solution No. II.

a. Weight of $Na_2SO_4$ in 25 c.c., 0·2636 grm.
b. Weight of $Na_2SO_4$ in 25 c.c., 0·2638 grm.

Weight of Na calculated from an average of the weights of $Na_2SO_4$ obtained in the above determinations, 0·0854 grm.

To determine the effects of the electric current upon solutions of hydrosulphide of sodium, 100 c.c. of the solu-

tion of sodium hydroxide were supersaturated with hydrogen sulphide, diluted to 400 c.c. by addition of water, and treated for about eleven hours with a three-ampère current. Considerable sulphur separated. This was filtered off and enough water added to make 1000 c.c. During the electrolysis some of the sulphur was oxidised to sulphuric acid, as was shown, both by the use of blue litmus paper and by a quantitative determination with barium chloride in hydrochloric acid solution. In all, two solutions, like the one just described, were prepared and analysed as before, with the following results :—

### Solution No. I.

*a*. Weight of $Na_2SO_4$ in 25 c.c., 0·2648 grm.
*b*. Weight of $Na_2SO_4$ in 25 c.c., 0·2638 grm.

Weight of sodium calculated from an average of the weights, $Na_2SO_4$ obtained in the above determinations, 0·08545 grm.

### Solution No. II.

*a*. Weight of $Na_2SO_4$ in 25 c.c., 0·2636 grm.
*b*. Weight of $Na_2SO_4$ in 25 c.c., 0·2640 grm.

Weight of sodium calculated from an average of the weights of $Na_2SO_4$ obtained in the above determinations, 0·08545 grm.

Determined by standard acid, the sodium in 2·5 c.c. solution of sodium hydroxide was 0·0860 grm. The sulphate method gave, as an average of duplicate determinations, 0·0858 grm. and the average of 0·0860 grm. and 0·0858 grm. is 0·0859 grm., the weight of sodium in 2·5 c.c. of the solution of sodium hydroxide.

This weight, 0·0859 grm., should correspond to the weight of sodium in 25 c.c. of the solution after electrolysis, if the oxidation of the sulphur compounds to sulphate is complete. For the sake of a better opportunity for comparison, the figures already obtained by analysis have been inserted below in a group.

Sodium in 2·5 c.c. NaOH solution, 0·0859 grm.

### Solution of $Na_2S$ after Electrolysis.

Sodium in 25 c.c. of No. I., 0·0857 grm.
Sodium in 25 c.c. of No. II., 0·0854 grm.

### Solution of NaSH after Electrolysis.

Sodium in 22 c.c. of No. I., 0·08545 grm.
Sodium in 25 c.c. of No. II., 0·08545 grm.

While the weights of sodium found in 25 c.c. of the solutions after electrolysis do not exactly agree with the weight found in 2·5 c.c. of the solution of sodium hydroxide, the agreement is so close that the complete change of sulphide and hydrosulphide to sulphate by electrolysis seems certain.

By what chemical change or changes is sulphate of sodium produced from sodium sulphide electrolytically? During the electrolysis of sulphide solutions, in the apparatus before described, some information on this point has been obtained by inspection. As soon as the current began its work electrolytic hydrogen escaped rapidly from the solution about the negative electrode. On the other hand, very little oxygen escaped at the positive. After the current had passed for a short time, the solutions, nearly colourless at first, grew yellow about the negative electrode, and the yellow colour rapidly diffused throughout the electrolyte. Later light yellow sulphur made its appearance on the positive electrode. It scaled off, however, as the electrolytic process proceeded, and the greater part dissolved in the surrounding liquid. Next, in order, fine white sulphur separated in little clouds about the positive electrode, near the surface of the liquid, but dissolved completely as it sank toward the bottom of the beaker cell. With the continuation of the electrolytic process, the clouds of fine white sulphur became larger and denser, so that immediately before the yellow colour disappeared from the electrolyte altogether, they did not dissolve, but gradually diffused

throughout the liquid and finally settled down upon the bottom of the beaker. At this stage of the electrolysis, and a little later, much more oxygen escaped from the solution than at any previous time during the passage of the electric current. The solutions were gradually warmed by the electrolytic action.

Taken up in reverse order, the phenomena above described are to be interpreted as follows :—The fine white sulphur separating in little clouds about the positive electrode, shows that sodium thiosulphate, $Na_2S_2O_3$, is present and being oxidised to sulphate in the electrolyte, while the light yellow sulphur, which adheres at first to the positive electrode, indicates the presence of polysulphides. These assertions rest upon the data collected during the electrolysis of sodium polysulphide and thiosulphate solutions in the apparatus already described. By such experiments it has been found that the sulphur from a thiosulphate solution always comes down finely divided and white, and does not adhere closely to the positive electrode. In a polysulphide solution, on the other hand, it clings tightly to the positive electrode at first, later scales off, and is light yellow in colour. The yellow colour of the electrolyte also indicates the presence of polysulphides. Again, after filtering off the precipitate formed by adding excess of ammoniacal zinc solution, the filtrate always gives the reactions of thiosulphate, on addition of an acid, provided the electrolysis is broken off after the little clouds of white sulphur begin to separate. The oxidation of sodium sulphide and hydrosulphide to sulphate is complete when the white sulphur separates no longer at the positive electrode. As for the electrolytic hydrogen, since it escapes from the electrolyte, it could not have acted chemically upon any substance therein. Moreover, if it had acted chemically, it must have acted as a reducing agent, in which event, from the nature of the substances in the liquid, sulphur would probably have separated at the negative electrode instead of the positive, just as it does in the electrolysis of aqueous solutions of sulphur dioxide, or would have combined with the liberated hydrogen to form hydrogen sulphide. But nothing of the sort happens. On the other hand, since electrolytic oxygen does not escape from the electrolyte, at least not during the first stages of the electrolysis, it must combine chemically to oxidise some substance or substances in the solution. It would seem very probable, therefore, that the oxidation of sodium sulphide and hydrosulphide to the sulphate is not retarded to any extent, at least, by the presence of electrolytic hydrogen, in which event the oxidation might be expected to go on, except so far as rate is concerned, in very much the same way that it does when air is drawn through solutions of sodium sulphide.

(To be continued).

# NOTICES OF BOOKS.

*Elementary Practical Chemistry and Qualitative Analysis.* By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., F.I.C., Head of the Chemical Department, South-West London Polytechnic. London: J. and A. Churchill. 1896. Post 8vo., pp. 224.

THE work before us, as we are informed in the authors' preface, is founded on a larger treatise on qualitative analysis with the addition of a special section experimentally illustrating the leading principles of chemical science.

The work commences with a list of apparatus required for each work-table in the laboratory of a college, the preparation and uses of apparatus, experiments showing the preparation of some gases and liquids, chemical

operations shown experimentally, and experiments involving weight and measurement.

Then follow analytical reactions. The reactions for metals, arranged in the usual groups; the reactions for acid radicles; the analysis of simple substances containing only one metal and one acid radicle; and a full analytical course with tables.

The appendix contains a list of chemical elements, atomic weights, equivalent weights, thermometric scales, weights and measures, and a list of formulæ.

This book, along with many others, may well be termed good seed, but when may we expect to reap the harvest, instead of importing it from Germany?

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*The Derivatives of Naphthalin which possess Technical Interest, arranged as a Conspectus.* (" Die Derivate des Naphthalins welche für die Technik Interesse, besitzen übersichtlich zusammengestellt.") By ERNST TAÜBER and RAGNAR NORMAN. Berlin: R. Gaertner's, Publishers. 1896. Pp. 219.

THE German scientific press does not, like our own, overflow with manuals and epitomes each of which bears a strong family likeness to the rest. But in return it is rich in monographs and in original works of well-marked technical value.

The appreciation of theory met with on the other side of the North Sea has more than justified itself in practice.

The contents of the work before us have appeared in the *Chemische Industrie*, and then as an independent pamphlet.

The authors treat successively of the amidonaphthalinesulpho acids, and of the oxynaphthalinesulpho acids, the diamidonaphthalines, the diamidonaphthalinesulpho acids, the dioxynaphthalines and their sulpho acids, the amidooxynaphthalines and their sulpho acids. To each of these sections is added a copious appendix.

Then follows a view of the literature of the subject, giving in parallel columns the name of the inventor, the journal in which the original work appeared, and the chief abstracts. Next we have a tabular view of the di- and tri-, the naphthalindi-, tri- and tetra-sulpho acids, the mononitronaphthalin, mono-, di- and trisulpho acids of known constitution.

Then follows an alphabetical list of those commercial or " trivial " names which do not indicate to what group the compounds in question belong.

In an appendix we have a list of publications which appeared whilst the body of the work has been printed.

Lastly comes a list of applications for patents which have been accepted; another list of those for which protection has been refused; and another list of such as have in the meantime expired.

Concerning the value of this work it is almost superfluous to speak. To chemists concerned with the manufacture, the use, or the investigation of the artificial colours, it will be found of the utmost utility.

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*A Short History of the City and Guilds of London Institute for the Advancement of Technical Education.* London : City and Guilds of London Institute. 1896.

FROM this pithy pamphlet we learn that the first step towards the formation of the City and Guilds of London Institute took place not less than twenty years ago, the main object being " to educate young artizans and others in the scientific and artistic branches of their trades."

The next year a provisional committee was formed, and it was resolved that the object in view would best be attained by the establishment of a Central College for the advanced education of such as had already acquired a sufficient knowledge of science or the arts to enable them to profit by the instruction in the industrial applications

of these; secondly, by conducting examinations (!) in technological subjects: and thirdly, by the establishment of local schools for artizans and workmen. Mention was made, as a model to be aimed at, of the Federal Polytechnic School of Zurich.

The Presidents of the Royal Society, and of the Chemical Society, of the Institution of Civil Engineers, and the Society of Arts are recognised as *ex officio* members of the Institute and its managing committees. The number of day-students at the Central College is now 208, and of evening students 526.

The Technical College at Finsbury—a much more suitable locality than South Kensington—is also flourishing. The chair of Electrical Engineering is filled by Prof. S. P. Thompson, D.Sc., F.R.S., and that of Chemistry by Prof. P. Meldola, F.R.S. The day students number 210, and the evening students 926.

The amount subscribed by the Companies to these Institutions during the past eighteen years has been £480,800. We believe that, as regards our national industries, this is a much better investment than the millions swallowed by the School Boards. A glance at a Financial Table may edify those who think that the City Guilds spend their means in a series of dinners.

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*Beginners' Guide to Photography, showing how to Buy a Camera and how to Use it.* By A FELLOW OF THE CHEMICAL SOCIETY. Published by Perken, Son, and Rayment, 97, Hatton Garden, London, E.C.

HERE, in the compass of 217 pages, we have an excellent guide for all who are taking up photography, clear, simple, and yet sufficiently comprehensive. We are particularly gratified with the section on micro-photography, a branch of the subject which, so to speak, is too often allowed to fall to the ground between two stools.

The learner will find here all which can be obtained by verbal tuition; experience and observation must do the rest.

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*Chemistry at a Glance :* a Study in Molecular Architecture. By HERBERT B. TUTTLE. New York. 1896.

UNDER this title we have the first part of an elementary work on chemistry, treating exclusively on oxides, and running to the extent of 60 pages; other parts being to follow. We are of course unable to say whether a person ignorant of chemistry would, by a glance at this work, acquire a clearer and fuller knowledge of chemistry than he could by other means.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 2, July 13, 1896.

**Evaporation of Metals at the ordinary Temperature.**—H. Pellat.—With reference to M. Colson's cummunication (p. 49 of the current volume) on the " Action of Zinc on a Gelatino-Bromide Plate," the author mentions that he obtained quite similar results with steel four years ago. He ascribed these results to the influence of a metal upon the nature of the surface of another metal placed at a little distance (*Comptes Rendus*, xciv., p. 1247).

**Process for Photographing Objects in Relief and Depression, and vice versa.**—Ernest Moussard.—The author takes an impression of the object by moulding in plaster or paper, and photographs this impression, which

is the inverse of the original, taking care to place at the bottom the top of the mould to be photographed, putting in the frame the gelatino-bromide plate, with the glass above and the sensitive layer below, so as to obtain a negative proof of the mould, which is itself the negative of the object, and then operate as usual.

**Manner in which the X Rays occasion the Discharge of Electrised Substances.**—Emilio Villari.

**Action of Metallic Tubes and Discs upon the X Rays.**—Emilio Villari.—The action of the rays which strike the electroscope is not transmitted by the wire to the aluminium disc. In the case of a leaden disc struck by the rays on its paraffined side the discharge from the uncovered side can only be produced by the rays which turn round the edge of the disc and penetrate into its shadow.

**Action of the Röntgen Rays upon the Bacillus of Diphtheria.**—F. Berton.—The author has exposed cultures of the bacillus of diphtheria in broth to the Röntgen rays for 16, 32, and 64 hours. After each exposure the cultures were sown in broth and injected into guinea-pigs. A check culture was similarly re-sown and injected into two guinea-pigs. The results were negative. The animals died as rapidly in the one case as in the other. This result agrees with that obtained by Wade (*British Med. Journal*) and Minck (*Mün. Med. Wochenschrift*).

**Fusibility of Metallic Alloys.**—Henri Gautier.—The researches of Le Chatelier show the absolute identity of alloys with the mixture of a salt and of water, commonly known as solutions. The curves of solubility correspond to the curves of fusibility. Metallic alloys are bodies whose crystalline structure is perfectly recognised. Thus the alloys of tin with zinc, bismuth, and lead correspond to the case where no combination ensues. The alloys of copper with tin and antimony correspond, on the contrary, to the case of a combination. The author points out an error which has been reproduced in all chemical text-books. The fusion-point of antimony is given as near 430°, whilst in reality this metal melts only at redness; its point of fusion determined by the pyrometer is 632°.

**On Steel Diamonds.**—M. Rossel.—This paper requires the four accompanying figures. It seems to the author that the formation of diamonds by the absorption of carbon by iron at a very high temperature and crystallising out as diamond when cooling under high pressure receives a new confirmation, and the theory of the production of diamonds put forward by M. Moissan appears to us perfectly justified.

**Action of Silicon upon the Alkaline Metals, Zinc, Aluminium, Lead, Tin, Antimony, Bismuth, Gold, and Platinum.**—Emile Vigoureux.—From the point of view of their behaviour with silicon we may divide the metals into two groups: those which do not combine directly with this element and those which do thus combine. We may include in the former class the alkaline metals, zinc, aluminium, lead, tin, antimony, bismuth, gold, and silver. They dissolve it almost all more or less abundantly, and abandon it afterwards in the form of crystals. The metals capable of uniting directly with silicon to form silicides perfectly crystalline are iron, chromium, nickel, cobalt, manganese, copper, and platinum. The composition of iron silicide ($SiFe_2$) and of chromium silicide ($SiCr_2$) having been first established by Moissan I have afterwards recognised that for all crystalline silicides it is analogous, *i.e.*, $SiM_4$ (M being a monatomic metal). A certain number of these new compounds dissolve silicon, as do the metals, *e.g.*, copper silicide, platinum silicide.

**On the Double Cyanides.**—Raoul Varet.—These results and those obtained with mercury cyanide show that the double salts formed by the metallic cyanides properly so-called, on combining with the cyanides of the alkaline and alkaline earthy metals, have the same formation heat in the dissolved state when we consider one and the same group of salts. They cannot be dissociated by dialysis. These characters permit us to consider them as derivatives of acids which do not exist in the free state or are at least very unstable, like the argentocyanhydric acid. The different double cyanides are distinguished from each other less by the difference of their molecular arrangement than by their greater or less stability.

**Action of Water upon Formic Aldehyd. Application to the rôle of this Substance in Plants.**—Marcel Delépine.—The facts established seem worthy of excessive interest if we only reflect that formic aldehyd is considered as the first term of the assimilation of carbon by chlorophyllic vegetables. If we suppose that the above reactions effected chemically at high temperatures take place physiologically in the plant at ordinary temperatures we may deduce numerous consequences. To the transformations of methylic aldehyd already admitted we must add a new one, enabling us to conceive why this compound is so difficult to detect, being liable to multiform transformations. By its splitting up into formic acid and methylic alcohol we may explain the presence of these two bodies in plants. We see, further, how formic acid may exist free, being formed by the action of water without the presence of a base being necessary. By its decomposition into carbonic acid and methylic alcohol we see that the presence of the latter almost universal in green leaves is not necessarily correlative with that of formic acid. But the most important consequence is the supply of an excess of hydrogen with elimination of carbonic acid.

**Reduction of Crotonic Aldehyd.**—E. Charon.—This paper is not well suited for abstraction.

**Rapid Determination of Carbonic Acid in the Air and in Confined Places.**—M. Henriet.—(See p. 64).

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*Revue Universelle des Mines et de la Metallurgie.*
Series 3, Vol. xxxiv., No. 2.

**Use of Thioacetic Acid in Analysis in place of Hydrogen Sulphide**—MM. Schiff and Tarugi.—To effect a precipitation, we add the reagent to the solution of the metals in hydrochloric acid. We heat on the water-bath, keeping below the point of ebullition. The precipitate is collected after the liquid is cold. The following is the action of ammonium thioacetate on the most important metallic salts. From $1\frac{1}{2}$ to 2 c.c. of the reagent are generally sufficient to precipitate 0·5 to 1 grm. of a metallic salt.

*Arsenic.*—In the cold a whitish turbidity; in heat the arsenites and arseniates give a precipitate of arsenious sulphide.

*Bismuth, Copper, Tin.*—The salts of these metals are partially precipitated in cold, completely in heat.

*Lead.*—In the cold a deep red precipitate (chlorosulphide?), which is converted totally into black sulphide on heating.

*Silver.*—A black precipitate. Silver chloride dissolved in hot hydrochloric acid is completely converted into sulphide.

*Cadmium.*—The precipitation is often not complete until after cooling.

*Mercury.*—Mercuric salts behave like those of lead.

*Platinum.*—In the cold a red precipitate of indefinite composition, which is converted into sulphide if heated.

*Gold.*—Like platinum.

*Iron.*—Ferric salts are at once reduced to the ferrous state, when the action ceases.

*Chrome.*—The chromates are reduced to the state of chromic salts, upon which the thioacetate has no action.

*Aluminium, Manganese, Zinc, Nickel, Cobalt.*—The salts of these metals are not precipitated by the acetate in an acid solution.

No. 3.

**Chemical Analysis and Bacteriological Examination of Potable Waters.**—W. J. Mason.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 5, Vol. i., No. 5.

The only chemical matter contained in this issue is a memoir on the improvements recently introduced in the beet-sugar industry.

No. 6.

**Report by M. Aimé Girard on the Control of Agricultural Distilleries, as proposed by M. Sidersky.**—M. Sidersky, it appears, has been appointed a permanent inspector of the agricultural distilleries. There was considerable jealousy at his appointment, but the arrangement has been found to work well in practice. We should suggest, however, that such inspectors should, in case of resignation, be bound most stringently not to act as consulting experts in this department of chemistry. It is here mentioned that the work effected by M. Sidersky during the first two years of the commission entrusted to him are full of interest from a professional point of view.

**Report submitted by M. de Luynes on behalf of the Committee of Chemical Arts on M. Lefèvre's Treatise on Colouring Matters.**—This work, which supplies a serious deficiency in French chemico-technical literature, is divided into twenty chapters, each referring to a class of colouring matters. After expounding Witt's theory of chromospheres and chromogenes the author treats of the nitro- and azoxy-colours. Chapter III. comprises the study of the azo-colours, along with which are arranged the sulphone compounds of the amines, the phenols, and the amido-phenols. The chapter concludes with a complete table of the azo-colours hitherto known, and with an indication of colours on the fibre. There are here found figures showing the plant required in the manufacture of the azo-colours. In the other chapters of the first volume we find described with equal care all that pertains to the hydrazinic colours, the indamines, the indones, the oxindamines, the oxindones, the thiazines, the eurhodines, the safranines, and the indulines. The colours discussed in the second volume are all derived from the subjoined carbides, except the colours derived from the chinoleic bases. They are the colours derived from naphthalene, diphenylmethane and its homologues, triphenylmethane and its homologues, anthracene and its homologues. The last chapter but one is devoted to the artificial indigos. In short, this work, of more than 1600 pages, contains all that has been done or published on the artificial colouring matters.

**Report presented by M. Schützenberger on behalf of the Committee of Chemical Arts on G. Segny's Ozoniser.**—This apparatus is intended for the application of ozone for industrial, medical, and antiseptic uses. The condensation is effected by means of the electric effluve. The apparatus consists of three wide horizontal tubes of glass connected so as to form a single S tube traversed by air or oxygen.

## MISCELLANEOUS.

**Oil of Reseda Root.**—J. Bertram and H. Walbaum (*Journ. Prakt. Chemie*).—This oil is light brown, smells distinctly of horseradish, and boils under ordinary pressure at 255° with decomposition. Its specific gravity at 15° is 1·067. It is slightly dextro-rotatory.

**Examination of Crude Olive Oil.** — E. Dietrich (*Helfenberger Annalen*).—The oil often contains much stearic acid and almost always fluctuating proportions of glycerides. The former constituent is ascertained by the acid number and iodine number, and the latter by the saponification number.

**Brazilian and Carolina Monazite.**—Carolina monazite occurs in irregular crystals, some being as large as a grain of wheat, and requires crushing, for which reasons the Auer-Welsbach Company, of Berlin and Vienna, pre-

fers the Brazilian monazite which comes in the form of a fine sea-washed sand. A ton of Brazilian monazite sand, costing at present in Hamburg 119 dols., yields, when well worked out, from 20 to 25 kg. of pure thoria, which is worth from 2400 dols. to 3000 dols., according to degree of purity. Thorium oxide is now worth in Germany from 120 dols. to 150 dols. per kilogrm., according to purity, and Mr. Mason, Consul at Frankfort, suggests the establishment in the monazite region of this country of a laboratory "where by employing the most improved and economical methods, the monazite, including the poorer sands which have been concentrated by a process recently perfected, may be worked up, the thoria extracted and made available as a finished product in all countries where incandescent gas burners are manufactured."—*Engineering and Mining Journal.*

# THE CHEMICAL NEWS,

## Vol. LXXIV., No. 1916.

## THE HOMOGENEITY OF ARGON AND OF HELIUM.

### By Prof. W. RAMSAY and J. NORMAN COLLIE.

THE question of the homogeneity of argon has been discussed by Lord Rayleigh and one of us in their memoir on Argon (*Phil. Trans.*, A, p. 236, 1895). But at that epoch the data were not sufficiently numerous to enable us to arrive at very definite conclusions. The discovery of helium and the analysis of its spectrum by Runge and Paschen (*Sitzungsberichte d. Akad. d. Wissenschaften*, pp. 639 and 759, Berlin, 1895) lead to the thought that this body may be a mixture of two gases.

To elucidate this question we submitted these two gases to a methodical diffusion, causing them to traverse a duct of porous pipe-clay submitted on one of its surfaces to the action of a vacuum. We satisfied ourselves that we might thus effect the separation of hydrogen and helium and that of oxygen and carbonic acid, and that, by measuring the rapidity of the descent of a column of mercury introduced in the circuit of the apparatus, it is possible to arrive at a good determination of the molecular weight of various gases. We have then tried to separate argon into two parts by a method analogous to the separation of liquids by fractionated distillation.

The quantity of argon was close upon 400 c.c. The gas was then treated in the manner shown in the following scheme :—

|  | More diffusible. | | | | | | Less diffusible. |
|---|---|---|---|---|---|---|---|
| I. | $\frac{1}{2}$ | .. .. | | | | .. .. | $\frac{1}{2}$ |
| II. | { $\frac{2}{3}$ $\frac{1}{2}$ | .. .. .. .. | $\frac{1}{3}$ | $\frac{1}{3}$ | | .. .. .. .. | $\frac{2}{3}$ $\frac{1}{2}$ } |
| III. | { $\frac{2}{3}$ $\frac{1}{2}$ | .. .. .. .. | $\frac{1}{3}$ | $\frac{1}{3}$ | | .. .. .. .. | $\frac{2}{3}$ $\frac{1}{2}$ } |
| IV. | $\frac{2}{3}$ $\frac{1}{2}$ | .. .. .. .. | $\frac{1}{3}$ | $\frac{1}{3}$ | | .. .. .. .. | $\frac{2}{3}$ $\frac{1}{2}$ |

We determined the density of the two extreme portions, and found that the one which ought to be the lightest had the density (O = 10) of 19·93, and the heaviest of 20·01. The separation, if it takes place, is therefore minimal.

The same experiment executed with helium yielded other results. The density of the specimen which passed first was 1·874, and that of the gas remaining in the apparatus 2·133. A great number of fractionations did not change these figures ; even the spectra of the two specimens were absolutely identical. Even the first bubbles of the lighter gas showed the same lines, with the same intensity, as the last bubbles which remained in the apparatus. There was no difference in fifty fractions.

Lord Rayleigh has had the kindness to measure the refraction of the two specimens of gas. Whilst the lighter gives the figure 0·1350 (atmospheric air = 1), the heavier had a refraction expressed by the figure 0·1524. Now these two numbers have a relation almost identical with the relation of the densities, for—

$$\frac{0\cdot1350}{0\cdot1524} = \frac{1\cdot874}{2\cdot110} \text{ in place of } \frac{1\cdot874}{2\cdot133}.$$

Let us now consider what happens when we submit a mixture of the two gases to diffusion. Let us take, *e. g.*, a mixture of hydrogen with an excess of oxygen. After a sufficient number of operations we obtain pure oxygen on the one hand, and on the other a mixture of 1 part o

hydrogen with 4 parts of oxygen. It will not be possible to separate this mixture into its constituents, on account of the equal diffusion of oxygen and hydrogen when thus mixed. The identity of the spectra of helium prevent us from deciding which is the pure gas and which is the mixture. Calculation establishes that if we suppose the heavier gas is a mixture, the density of the lighter, supposed pure, ought to be 1·58. Helium, lastly, if it consists of a mixture of two gases, is formed either of two gases of the densities 2·366 and 1·874, or of two gases of the densities 2·133 and 1·580.

But although this explanation is the most suitable, there exists another which deserves our attention. The spectrum of these two fractions shows no difference. It is not probable that two gases exist the densities of which are so near each other. The different gases do not possess a refraction proportional to their densities. It seems to us that we might admit that we have effected a real separation of the light mols. from the heavy mols. The idea that all the mols. of a gas are homogeneous has never been submitted to the test of experiment. We do not know of any attempt at a separation of this kind of a gas regarded as homogeneous into two different parts. But our experiments show that this question deserves to be studied. If it can yield us similar results we must change our ideas on the nature of matter.— *Comptes Rendus*, vol. cxxiii., p. 214.

## A NOTE ON THERMOMETERS.

### By Dr. T. L. PHIPSON.

FOR some time past it has been part of my laboratory work to examine thermometers used in the rooms of invalids, as well as some constantly employed for industrial purposes or for meteorological observations.

All physicists are aware how necessary it is to test, now and then, all kinds of thermometers, even those of the best makers, in order to take into account any erroneous indication which may be the result of dilatation or contraction of the glass reservoir. But errors of this kind are, according to my experience, not very common, and rarely reach to 1° C. in a well-made instrument. Nevertheless, it is necessary to know them ; and for this purpose all new thermometers used for scientific research should be examined at least once a year, until they are found to be invariable.

Clinical thermometers having a very limited scale, and being, as a rule, most carefully made, do not appear so liable to error as the ordinary laboratory thermometer. Two clinical thermometers, made in London, which have been used by me for the last fifteen years, have not varied one with the other in the slightest manner during the whole of that time.

The ordinary laboratory thermometer is supposed to be thoroughly tested by the makers, and is sometimes guaranteed ; nevertheless, the discrepancies noted in boiling-points and melting-points, given by chemists of high standing, appear to indicate that a faulty thermometer is more likely to be the cause of these discrepancies than inexperienced manipulation or impurities in the substance examined.

With regard to thermometers used in the sick room, and in the household generally, I have found very great differences. In such cases cheap instruments, which have not been thoroughly tested, are in frequent use ; and the employment of an inexact thermometer in the sick room is not devoid of danger. For instance, a patient 80 years of age, suffering from bronchitis, did not cough or suffer from prostration when the thermometer registered 68° to 70° F., but fell into an alarming state of prostration when it rose to 72° or 73°. Now many thermometers, both mercurial and spirit, which I have examined of recent years, have shown errors of 4° or 5° F., and sometimes

even more, and it is very essential that all such instruments used for taking the temperature of sick rooms or hospital wards should be carefully compared from time to time with a standard instrument of known accuracy, or otherwise tested, so that their amount of error may be exactly known.

The same observation holds good, of course, for thermometers used in registering the temperature of the air. In this case two things are most requisite : 1st, an absolutely correct thermometer ; and 2nd, that the observation be invariably made at the same hour. Without these conditions are fulfilled such observations are absolutely worthless. For some time I have been puzzled by the exceedingly high temperatures published in *The Standard* as regards the town of Calais, in the daily list of European localities for which the temperature is given at 9.30 a.m. Calais, in this list, invariably registers much higher than Ostend, Dieppe, or Boulogne, which are all in the same neighbourhood on the map of Europe. There is often a difference of more than 10° F. It would be interesting to enquire into the cause of this, as Calais is said to be near the centre or pivot of an upheaval oscillation described by some geologists. But I fear the discrepancy in question may be due simply to a faulty thermometer in use at that place, or that the temperature is not taken strictly at 9.30 a.m.,—though, in these days of accurate scientific work, it is almost impossible to imagine such a thing.

During the severe and prolonged frost of January and February, 1895, a meteorologist in Surrey recorded the temperature at 9.30 a.m. and 9.30 p.m. every day. He used for this purpose an expensive mercurial thermometer. But when I examined this instrument later, I found that it registered 4° F. too high.

As the thermometer is an instrument daily in use, not only in the chemical laboratory and manufactories, but by the physician, the meteorologist, the brewer, the sanitary engineer, and in a host of industries, and as the indications of a faulty instrument (unless the error is known) are not merely worthless, but often costly and dangerous, it may be advantageous to bear in mind the subject of this short note.

The Casa Mia Laboratory, Putney.

# ESTIMATION OF SULPHUR IN CAST-IRON OR STEEL.

## By G. G. BOUCHER.

FIVE grms. of iron or steel are dissolved in a strong solution of copper ammonium chloride, and when the precipitated copper is dissolved the solution is filtered. The filter-paper and contents are then thoroughly washed with hot distilled water till the washings are free from copper. The sulphur remains on the paper with the graphite and a small quantity of silica and iron. The paper and contents are now placed in a small beaker, and about 30 c.c. of nitro-hydrochloric acid are added ; the solution is then boiled and filtered ; the filtrate is neutralised with ammonium hydrate, and then made slightly acid with dilute hydrochloric acid. To the solution 5 grms. of barium chloride are now added; the solution is heated, and the barium sulphate allowed to settle. It is then filtered off, well washed, burnt, and weighed.

Instead of dissolving the sulphur out of the residue of graphite, &c., with nitro-hydrochloric acid, the paper and contents may be boiled with bromine-water and a few drops of hydrochloric acid. When the excess of bromine has been boiled off the solution is filtered, and barium chloride added to the filtrate. The solution is heated, &c., as before.

Below I give a few analyses by this process :—

| | | Nitro-hydrochloric acid method. Sulphur p. c. | Copper-ammonium chloride method. Sulphur p. c. |
|---|---|---|---|
| 1. | Bessemer iron .. | 0·035 | 0·041 |
| 2. | ,, | 0·012 | 0·021 |
| 3. | ,, | 0·022 | 0·024 |
| 4. | ,, | 0·023 | 0·023 |

| | | | 1st anal. | 2nd anal. |
|---|---|---|---|---|
| 5. | ,, | — | 0·020 | 0·021 |
| 6. | Mottled iron .. | 0·185 | 0·192 | 0·192 |

This processs is particularly adapted for the estimation of small quantities of sulphur, the absence of a large quantity of ferric chloride, and free hydrochloric acid in which barium sulphate is soluble to an appreciable extent, rendering the process extremely accurate.

The percentage of sulphur obtained by this process is higher than that given by any other processes I know of, and the barium sulphate is always white, showing the absence of iron.

The Laboratory, North Lonsdale Iron Works,
Ulverston, August 3, 1896.

# ON THE CONTENTS OF PHOSPHORUS AND SULPHUR IN CRUCIBLE STEELS.

## By SERGIUS KERN, M.E., St. Petersburg.

I THINK the following table, drawn out by me after many years of work with crucible steels, the manufacture of which has been my special care, may be of some use to metallurgists.

*Formula for the Contents of Phosphorus + Sulphur in Crucible Steels.*

| | P+S. Joint per cent. |
|---|---|
| Tool Steel— | |
| Best .. .. .. .. .. .. | 0·03 |
| Fair .. .. .. .. .. .. | 0·04 |
| Middling (rather suspicious) | 0·05 |
| Projectiles .. .. .. .. .. | 0·03 |

In this sum it is preferable to have the sulphur as low as possible, say, 0·19 per cent (maximum). This was the strong convincement of my good friend of my good friend the late M. Antoine Rollet.

| | P+S. Joint per cent. |
|---|---|
| Steel Castings— | |
| Best .. .. .. .. .. .. | 0·05 |
| Fair .. .. .. .. .. .. | 0·08 |
| Suspicious .. .. .. .. | 0·10 |

All castings to be imperatively annealed.

# JAPANESE COAL.

## By FRANK BROWNE, F.C.S., Acting Government Analyst, Hongkong.

THE sample examined was that variety known as Tubari coal, from the island of Yezo. It was in large black lumps, which when broken up gave a dark chocolate-brown powder. It burned readily, giving at first a bright smoky flame, which disappeared after a short time, leaving a glowing mass. It is a non-caking coal. The results of the analysis show high percentages of volatile combustible matter and of ash.

It consisted of—

| | |
|---|---|
| Moisture .. .. .. .. .. | 3·83 |
| Volatile combustible matter .. | 36·62 |
| Fixed carbon .. .. .. .. | 42·70 |
| Ash .. .. .. .. .. .. | 16·85 |
| | 100·00 |

Ultimate analysis of the dried coal gave—

| | |
|---|---|
| Carbon .. .. .. .. .. .. | 62·84 |
| Hydrogen .. .. .. .. .. | 6·37 |
| Nitrogen .. .. .. .. .. | 1·08 |
| Oxygen (calculated) .. .. .. | 11·01 |
| Sulphur (combustible) .. .. | 1·18 |
| Ash (containing 0·49 per cent of sulphur) .. .. .. .. | 17·52 |
| | 100·00 |

The relative density (water at $15\cdot5° = 1$) was 1·411.

The heat of combustion calculated from the following formula—

$$8080 \; C + 34462 \; (H - o/8) + 2220 \; S$$

gave 6826 calories.

## ON THE
## EXISTENCE OF PENTAETHYL NITROGEN.*

### By ARTHUR LACHMAN.

THERE is *à priori* no reason why nitrogen in its pentavalent state cannot combine with five *like* atoms or radicals, just as in its trivalent state it unites with three like atoms. And there is, further, no reason known why in pentavalent nitrogen compounds the atoms or radicals attached to the nitrogen must consist of two groups, strongly contrasted ($e. g.$, $H_4 \equiv N - Cl$, $(CH_3)_3 \equiv N = ICl$, $C_6H_5 - N \equiv O_2$). The existence of a compound $NX_5$, therefore, is not contradicted by anything but experience, and it seemed well worth the effort to attempt its preparation. The pentachloride, $NCl_5$, was not to be thought of; the hydrogen compound, $NH_5$, presented no point of attack; but for the pentaethyl compound, $N(C_2H_5)_5$, one method in particular suggested itself, which has been very frequently employed in the carbon series, and which had been successful in the one case where it was tried with (trivalent) nitrogen.

This method is the action of zinc alkyl on alkyl halogen substitution products of the hypothetical compound, $NH_5$. Tertiary butyl iodide (*Ann. Chem.*, Liebig, clxv., 107), $(CH_3)_3CI$, reacts immediately with zinc ethyl, and tetraethylammonium iodide, $(C_2H_5)_4NI$, seems to be structurally analogous. Triethylamine dibromide,†—

$$(C_2H_5)_3NBr_2,$$
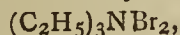
appears to present even a more favourable case, as Tscherniak (*Ber. d. Chem. Ges.*, ix., 143) had successfully prepared triethylamine by the action of zinc ethyl on ethyldichloramine, $(C_2H_5)NCl_2$. The experiments were confined to these two substances.

### *Action of Zinc Ethyl on Tetraethylammonium Iodide.*

Strange to say, tetraethylammonium iodide and zinc ethyl do apparently react. The action is very slow; heating on the water-bath for several hours produces no effect, nor does standing at ordinary temperature for ten days. But if, after standing from four to six weeks, a mixture of the substances in question (slightly diluted with ether to give fluidity to the mass) is poured into water and filtered from the zinc hydrate‡, the solution possesses a *strongly alkaline* reaction. It slowly turns yellow, and then a finely crystalline red precipitate separates. This precipitation is not hastened by carbon dioxide; in the experiment that was carefully controlled it required a day and a half for completion.

Ten grms. tetraethylammonium iodide, 5 grms. zinc ethyl, and 15 c.c. ether, stood for forty-three days at the ordinary working temperature, and yielded 0·61 grm. of the red substance. This red substance, by properties and analysis, seems to be tetraethyl ammonium triiodide, $(C_2H_5)_4NI_3$. (Found 73·4 per cent iodine, calculated 74·5 per cent; the crude product was analysed directly).

I am at a loss to explain this curious reaction. The formation of an alkaline* substance is in itself peculiar. The alkaline body could not be isolated nor in any way identified, owing to the very small quantity formed; in evaporating the solution saturated with carbon dioxide, the alkaline reaction disappeared. The precipitation of tetraethylammonium triiodide from an *alkaline* solution, which could not have contained any free iodine, is quite inexplicable.

### *Action of Zinc Ethyl on Triethylamine Dibromide.*†
This reaction presented three possibilities :—

I. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_5N + ZnBr_2.$
II. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_4NBr + Zn(C_2H_5)Br.$
III. $(C_2H_5)_3NBr_2 + Zn(C_2H_5)_2 = (C_2H_5)_3N + C_2H_5Br + Zn(C_2H_5)Br.$

Reactions I. and II. would represent actual syntheses; reaction III. would involve reduction. Experiment showed that reaction III. took place to the exclusion‡ of the others. It seems superfluous to give the details of work which has no preparative value; but every product of the action was identified. As a matter of fact, in some cases where the mixture of zinc ethyl and the dibromide (always diluted with considerable chloroform) was allowed to stand several hours, as much as 33 per cent of the total nitrogen employed was obtained as tetraethylammonium bromide; but this was due to a secondary action,—the addition of ethyl bromide to triethylamine,—for, if the mixture was examined shortly after its preparation, no quaternary ammonium compound could be found.

No synthesis whatever, then, had been accomplished. Triethylamine dibromide, in its action toward zinc ethyl, behaves merely as a mixture of triethylamine and bromine. It will be interesting to learn from Dr. Norris whether it behaves thus in every case. In this connection it may be remarked that ethyl dichloramine, which reacts normally with zinc ethyl, acts like free chlorine in some instances (*Ber. d. Chem. Ges.*, xvi., 1047).

Perhaps pentaethyl nitrogen will be prepared by some one more fortunate, by means at present undiscernible. The experiments just sketched will not be continued.

### *Action of Zinc Ethyl on Phenyl Iodide Chloride.*

This may be the place to briefly give an account of the action of zinc ethyl on phenyl iodide chloride, $C_6H_5I.Cl_2$, which possesses some analogy to triethylamine dibromide, and the study of which I took up for that reason. Both are halogen addition-products, a sort of half-way station between the more stable derivative of elements exhibiting two valencies. One might reasonably expect to obtain, in this case, a semi-aliphatic analogue,—

$$\genfrac{}{}{0pt}{}{C_6H_5}{C_2H_5} > ICl,$$
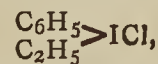
of the very stable iodonium compounds of Hartmann and Victor Meyer. The reaction, however, is exactly analogous to that of the dibromide: phenyl iodide, ethyl chloride,

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† The kindness of Dr. J. F. Norris enabled me to use this compound instead of the more difficultly accessible $(CH_3)_3NICl$.
‡ It was impossible to determine satisfactorily whether this zinc hydrate contained basic zinc iodide, and thus ascertain whether the zinc ethyl had reacted in the usual manner. The hydrate retained tetraethylammonium iodide so tenaciously that even after washing for several days with water and alcohol the filtrate still gave a distinct reaction with silver nitrate.

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* It is not impossible that this alkaline substance is really pentaethyl nitrogen, but alkalinity is hardly a property it would be expected to possess.
† This was prepared according to Remsen and Norris. *American Chemical Journal*, xviii., 90.
‡ A minor reaction, represented by the equation —
$$(C_2H_5)_3NBr_2 + Zn(C_2H_5)Br = (C_2H_5)_3N + C_2H_5Br + ZnBr_2,$$
also took place.

zinc chloride, and zinc oxychloride are the final products. There are indications that an unstable intermediate addition-product is formed. It was possible to show analytically that almost exactly half of the total chlorine was regained as zinc chloride (and oxychloride); the other half could not be accurately traced: the phenyl iodide was recovered unaltered, and in practically theoretical quantity, but only a small percentage of ethyl chloride could be isolated.

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## THE PREPARATION OF ALLYLENE, AND THE ACTION OF MAGNESIUM UPON ORGANIC COMPOUNDS.

### By EDWARD H. KEISER.

As described in a previous paper (*Journal of the Franklin Institute*, Jan., 1895) metallic magnesium at a low red heat acts energetically upon the vapours of the alcohols. The metal glows and is converted into a black coherent mass. This black residue, when put into water, evolves a gas which consists chiefly of hydrogen and allylene. The evolution of gas becomes very rapid if a few drops of ammonium chloride solution are added to the water. The hydrogen and allylene can be readily separated from one another by conducting the mixed gases through a series of wash-bottles containing an ammoniacal solution of silver nitrate; the allylene is thereby converted into the insoluble silver allylide, $AgC_3H_3$, while the hydrogen passes through unchanged.

The best yield of allylene in the earlier experiments was obtained from the magnesium that had been heated in the vapours of propyl or of allyl alcohols. Recent experiments have shown that a more advantageous method of preparing the hydrocarbon is to heat magnesium powder in the vapour of acetone, and to decompose the black mass thus obtained with water. In the method of preparation now adopted a layer of magnesium powder is put into a thin-walled iron tube, which is as long as the combustion-furnace that is to be subsequently employed for heating it. The iron tube is closed with asbestos stoppers, and through these stoppers glass tubes are passed; so that the acetone vapour may be conducted in at one end of the iron tube, and the gases formed during the reaction may be drawn off at the other end. The acetone is converted into vapour by boiling the liquid in a flask which is connected with one end of the iron tube containing the magnesium. After the air is driven out of the apparatus the iron tube is heated in the combustion-furnace. At a low red heat the action begins; the magnesium becomes red-hot, and finally the glowing extends throughout the entire mass of the metal. When this has taken place the contents of the tube are allowed to cool down in the acetone vapour; the black mass is then removed from the tube, and, since the moisture of the air acts upon it, it is best to preserve it in a tightly stoppered bottle. To obtain allylene from this residue it is only necessary to put it into a flask containing water to which a few drops of ammonium chloride solution have been added. The gas given off consists mainly of allylene and hydrogen, the latter gas being obtained from the magnesium that has remained unacted upon.

In order to throw light upon the nature of the reaction that takes place when magnesium acts upon the alcohols and upon acetone, the gases that escaped from the tube while the magnesium was glowing were collected in gasometers over water. These gases were analysed, and the results of the analyses are given in the following table. (See next column).

From the very small quantities of oxides of carbon in these gases it seems probable that the magnesium combines with the oxygen of the alcohols; hydrogen and hydrocarbons are thereby formed, and at the elevated

| Alcohols. | $CO_2$. | CO. | Unsaturated hydro-carbons. | Saturated hydro-carbons. | Hydro-gen. |
|---|---|---|---|---|---|
| Methyl | 0·8 | 0·6 | — | 19·7 | 78·9 |
| Ethyl | — | 0·4 | 14·0 | 11·1 | 74·5 |
| Propyl | — | 3·5 | 17·8 | 19·9 | 58·8 |
| Isopropyl | — | 0·2 | 12·2 | 15·4 | 72·2 |
| Isobutyl | — | 0·5 | 11·4 | 14·4 | 73·7 |
| Amyl | 1·0 | — | 20·4 | 22·3 | 56·3 |
| Tertiary amyl (a) | — | — | 24·3 | 17·5 | 58·2 |
| „ (b) | 0·2 | — | 22·4 | 17·9 | 59·3 |
| Secondary octyl (a) | — | 0·5 | 26·0 | 24·5 | 49·0 |
| „ (b) | 0·6 | 1·6 | 25·2 | 25·8 | 46·8 |

temperature of the reaction a portion of the magnesium unites with the carbon and hydrogen of these compounds, forming magnesium allylide. The black residue contains, besides the magnesium oxide and magnesium allylide, a quantity of free carbon. Attempts have been made to extract the allylide by means of solvents, but thus far it has not been possible to obtain a solvent for it. That magnesium allylide is present in the black mass is shown not only by the action of water upon it, whereby allylene is evolved which has been transformed into the silver, the mercury, and the copper compounds which characterise this hydrocarbon; but also by the fact that it contains from 0·3 to 0·4 per cent of hydrogen, as has been found by burning weighed quantities of it in a stream of oxygen. Further experiments have shown that when the magnesium is heated in an atmosphere containing no hydrogen, as, for instance, in carbon monoxide or carbon dioxide, and the residue thus obtained is decomposed by water, the gas evolved gives scarcely any precipitate with ammoniacal silver solution, the small traces of silver allylide thus obtained being formed from the hydrogen which is occluded in the metallic magnesium.

The black mass, consisting of magnesium oxide, carbon, and magnesium allylide obtained by the glowing of magnesium in the vapours of acetone and of the alcohols, was in each case treated with water, and the gases evolved were conducted through an ammoniacal solution of silver nitrate. The silver precipitates were removed by filtration, and, after washing and drying, were analysed. The following table contains the results of the analyses:—

| Magnesium allylide from | | Analyses of silver precipitates. | | |
|---|---|---|---|---|
| | | Wt. taken. | Wt. AgCl found. | Per cent Ag. |
| Acetone | | 0·1617 | 0·1577 | 73·40 |
| Methyl alcohol | | 0·1292 | 0·1270 | 73·97 |
| Ethyl „ | (a) | 0·1163 | 0·11365 | 73·53 |
| | (b) | 0·0979 | 0·09615 | 73·89 |
| Propyl „ | | 0·15605 | 0·1522 | 73·39 |
| Isopropyl „ | (a) | 0·27308 | 0·26802 | 73·58 |
| | (b) | 0·10244 | 0·10114 | 74·31 |
| Allyl „ | (a) | 0·16705 | 0·1620 | 72·97 |
| | (b) | 0·17185 | 0·16735 | 73·27 |
| Isobutyl „ | | 0·1301 | 0·1289 | 74·56 |
| Amyl „ | (a) | 0·18156 | 0·17933 | 74·34 |
| | (b) | 0·1365 | 0·13767 | 75·90 |
| Tertiary amyl „ | | 0·08509 | 0·08374 | 74·07 |
| Calculated for $AgC_3H_3$ .. .. .. .. .. | | | | 73·45 |

The comparatively close agreement of these results with the theoretical value for silver in silver allylide indicates that the silver precipitates were most probably pure compounds. The copper allylide was made by conducting the gases from the evolution flask through an ammoniacal solution of cuprous chloride. The greenish yellow precipitate was filtered and washed thoroughly with water, and, after drying in desiccators, was analysed.

Found 62·1 and 62·2 per cent of Cu.
Calculated for $CuC_3H_3$, 61·98 per cent.

The mercury allylide has also been prepared. When first formed it is a white flocculent precipitate. It was purified by dissolving it in boiling alcohol. On cooling it crystallised out in the form of slender needles. These crystals possessed the properties of the mercuric allylide described by Kutscheroff (*Ber. d. Chem. Ges.*, xvii., 26).

Experiments have also been made to determine the yield of allylene obtained by this method of preparation. If it be assumed that the magnesium acts upon the acetone vapour according to the following equation—

$$2C_3H_6O + 3Mg = 2MgO + Mg(C_3H_3)_2 + 6H,$$

then the residual magnesium mass should contain 3·3 per cent of hydrogen. Determinations of hydrogen by combustion gave on an average 0·37 per cent; so that the yield would be about 0·1 of the theoretical amount. Further, 10 grms. of the magnesium residue gave about 0·7 grm. silver precipitate.

Further experiments with the allylene are in progress. The gas is readily absorbed by concentrated sulphuric acid. It is probable that a sulphonic acid is thus formed. The sulphuric acid, after having absorbed a large volume of the gas, was diluted with water and neutralised with barium carbonate. After filtration the clear solution on evaporation gave a deposit of a crystalline barium salt. The composition of this compound is now being determined.

In conclusion, I desire to express my thanks to Miss Mary B. Breed and Miss Lucy Francisco for their careful work in making the analyses and in assisting me in the experiments described in this paper.— *American Chemical Journal*, vol. xviii., No. 4.

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## THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.*

By HENRY FAY.

(Concluded from p. 70).

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### Decomposition of Acetic Acid.

VARIOUS attempts were made to decompose acetic acid in the same manner as propionic and isobutyric acid, but it was decomposed only with difficulty. The only proportions which were found to give off gas was when 15 c.c. glacial acetic acid and 5 c.c. strong solution of uranyl acetate were exposed. From this solution gas was given off, but only extremely slowly. The exposure was made in April and May, about six weeks being required to give enough for analysis. The clear yellow solution did not to any extent change to the green, so characteristic in all the other cases. There was a slight green colour, but it was not marked.

Analysis of gas :—

13·4 c.c. of gas gave 6·4 c.c. CO₂.

| | | |
|---|---|---|
| Volume of original gas | 13·2 m.m. = 1 vol. | |
| Volume after addition of oxygen | 108·24 „ = 8·2 vols. | |
| Volume after explosion | 80·52 „ = 6·1 „ | |
| Contraction | = 2·1 „ | |

Calculated contraction for $CH_4$ is 2 volumes, while that found is 2·1 volumes, which shows the gas to be methane, and the decomposition is to be represented by the equation—

$$CH_3.COOH = CH_4 + CO_2.$$
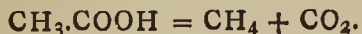
It is interesting to note that the power of decomposition ceases with acetic acid, which breaks down under

the influence of light only with difficulty. The power is apparently lost in formic acid, and it has been impossible so far to effect any decomposition of this acid by light in the presence of uranium salts.

### Comparison of the Rates of Decomposition of Propionic, Butyric, and Isobutyric Acids.

For the purpose of comparing the relative rates of decomposition of these three acids, tenth-normal solutions of each were made, and varying quantities of the acid were exposed with varying quantities of uranyl nitrate. It was decided to use propionic acid as the standard in determining the best conditions possible. The following table shows the comparison between two solutions of propionic acid exposed under exactly similar conditions :—

| No. of days. | Hours of exposure. | Amount of gas collected. No. 1. | No. 2. | Condition of weather. |
|---|---|---|---|---|
| 1 | 2 | 0·8 | 0·6 | Clear. |
| 2 | 7½ | 2·8 | 2·8 | „ |
| 3 | 7½ | 3·4 | 4·8 | „ |
| 4 | 7½ | 4·0 | 7·2 | „ |
| 5 | 15 | 4·3 | 9·2 | „ |

Solution No. 1 contained 10 c.c. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$, and 10 c.c. one-tenth normal propionic acid.

Solution No. 2 contained 15 c.c. one-tenth normal propionic acid and 5 c.c. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$.

It will be seen that the solution containing the larger amount of acid acted the more rapidly. The comparison is not exactly fair, as the precipitate, which is formed some time after the decomposition begins, has some effect, as will be seen in the following table, in which is given a comparison of propionic, butyric, and isobutyric acids. Each solution contains 15 c.c. one-tenth normal acid and 5 c.c. one-tenth normal nitrate, $UO_2(NO_3)_2.6H_2O$.

| No. of days. | Amount of gas collected. Propionic. | Isobutyric. | Butyric. |
|---|---|---|---|
| 1 | 1·2 | 1·4 | 1·0 |
| 2 | 2·5 | 3·0 | 2·5 |
| 3 | 4·0 | 4·7 | 3·6 |
| 4 | 5·3 | 5·7 | 4·3 |
| 5 | 5·3 | 5·7 | 4·3 |
| 6 | 6·5 | 6·4 | 4·9 |
| 10 | 7·6 | 7·4 | 5·8 |
| 11 | 8·8 | 8·4 | — |
| 12 | 10·2 | 9·5 | — |
| 13 | 12·0 | 10·6 | 9·0 |
| 14 | 13·6 | 11·4 | 9·6 |
| 15 | 15·0 | 12·4 | 10·5 |
| 16 | 15·8 | 12·8 | 11·2 |
| 17 | 16·3 | 13·0 | 11·2 |

It will be seen that on the sixth day the amount of gas collected from the propionic acid and the isobutyric acid is practically the same. Up to this time there was only slight cloudiness in the solutions, but after three days of rain a precipitate was found in the solution containing isobutyric acid. From this time on it will be seen that there is a gradual gain in the amount of gas collected from the propionic acid over the amount collected from the isobutyric acid.

As the weather was unfavourable for carrying these comparisons any further, the subject was dropped at this point, but it is believed that interesting comparisons can be obtained by working during the summer months.

### Summary.

It has been shown that the precipitate in the solution of uranyl oxalate and oxalic acid is formed in two stages: (1) formation of uranous oxalate, (2) formation of the purplish brown precipitate from the uranyl oxalate left in solution. The nature of the latter has not been cleared

up, but it is shown to contain carbon, and consequently cannot be the hydrated oxide as supposed. The formic acid found when oxalic acid is decomposed must come from the oxalic acid itself, as all attempts to build it up from water and carbon monoxide in presence of uranium salts have failed.

Tartaric acid, when exposed with uranium salts to the sunlight, forms an insoluble precipitate with uranium, the nature of which has not been cleared up.

It has finally been shown that acetic, propionic, and isobutyric acids decompose into the hydrocarbons corresponding to the acids and into carbon dioxide.

# OXIDATION OF SODIUM SULPHIDE AND HYDROSULPHIDE TO THE SULPHATE BY ELECTROLYSIS.*

By FRANK W. DURKEE.

(Concluded from p. 71).

DRAWING air through solutions of sodium sulphide, according to Lunge ("Soda Industry," p. 531), first produces sodium hydroxide and sodium thiosulphate, $2Na_2S + 4O + H_2O = 2NaOH + Na_2S_2O_3$. The thiosulphate then takes oxygen from the air and forms sodium sulphate, and sulphur separates, $Na_2S_2O_3 + O = Na_2SO_4 + S$. Afterwards yellow polysulphides result from the solution of the free sulphur in sodium sulphide and hydroxide, come in contact with more oxygen, sulphur separates again, and an additional amount of thiosulphate is produced, $Na_2S_5 + 3O = Na_2S_2O_3 + 3S$ (Dopping, *Ann. Chem.* (Liebig), xlvi., 172). Very likely other polysulphides are produced, but are all changed to the thiosulphate by the free oxygen, according to similar reactions.

If, therefore, the electrolytic oxidation of sodium sulphide to the sulphate takes place as above described, at any instance after the electric current has acted on the solution for some time, and, indeed, until very near the end of the electrolytic oxidation, the sum of the weights of sodium in the sulphide, hydroxide, sulphate, thiosulphate, and polysulphide, must equal the weight of sodium in the solution of sodium sulphide before electrolysis. Moreover, if these weights do equal each other, it follows that the oxidation takes place through the formation of these compounds and no others. So, to settle the point under consideration, it is only necessary to subject solutions of sodium sulphide to electrolytic action for different periods of time, and then to rigorous quantitative analysis, in order to determine whether the oxidation takes place according to the above reactions or not.

For convenience, the sulphide solutions, intended for analysis and described below, have been numbered.

Number I. was prepared by supersaturating with hydrogen sulphide 50 c.c. of the solution of sodium hydroxide, already described and analysed, and adding 50 c.c. more of the same solution of sodium hydroxide. After diluting with 300 c.c. of water, the solution was subjected to electrolysis, in the apparatus before used. A 3·1 ampère current passed for one hour and thirty minutes, after which the solution was filtered and made up to 1000 c.c. by addition of water. Numbers II., III., IV., and V. were prepared by the method used in the preparation of No. I., but the electric current and time of electrolysis varied in each case. No. II. was subjected to the action of a 3·1 ampère current for two hours; No. III. to a 3·2 ampère current for two hours and thirty minutes; No. IV. to a 3·0 ampère current for two hours and thirty minutes; No. V. to a 3·1 ampère current for six hours and forty minutes. As a high-reading ampère metre was used a part of the time, in some cases, the above figures representing ampères may not be entirely reliable.

In 50 c.c. of the electrolytes, which, theoretically contain as much sodium as 5 c.c. of the solution of sodium hydroxide, the determination of sodium in the different compounds has been made by the following analytical methods:—To get the weight of sodium in the sulphate, hydrochloric acid and barium chloride have been added to 50 c.c. of the electrolytes, and the resulting barium sulphate determined in the usual way. The weight of sodium in sodium sulphate has then been calculated from the weight of barium sulphate obtained.

The weight of sodium in sulphides has been obtained by use of standard zinc solution, prepared by dissolving 3·253 grms. of pure zinc in hydrochloric acid and adding ammonia to supersaturate the liquid. Enough water was then added to make 1000 c.c. Nickel nitrate upon a white plate has been used as indicator in these titrations.

The first step in the method used for the determination of sodium in the form of the thiosulphate has been to add to the solution a slight excess of the zinc solution described above. The resulting sulphide of zinc and free sulphur have then been filtered off, excluding the air as much as possible meanwhile, and excess of bromine has been added to the filtrate to oxidise the thiosulphate to acid sulphate. After acidifying with hydrochloric acid, an excess of barium chloride has been added, the weight of the barium sulphate afterward determined in the usual way, and from it the corresponding weight of sodium calculated. By subtracting from this the weight of sodium found in sodium sulphate, twice the weight of the sodium combined in the thiosulphate has been obtained.

In the determination of sodium in the form of hydroxide, a large excess of standard sulphuric acid has been added to 50 c.c. of the electrolyte solutions. Afterwards they have been rapidly boiled to expel sulphur dioxide and hydrogen sulphide, filtered, and titrated back with standard sodium hydroxide, using methyl-orange in cold solution as indicator. By subtracting the weight of the sodium in the standard solution of sodium hydroxide used, from the weight of sodium that the standard sulphuric acid would neutralise, the weight of sodium acted upon by the standard sulphuric acid in the electrolyte solution under examination has been obtained. The difference between this weight of sodium and the sum of the weights of sodium in sulphides and thiosulphate equals the weight of sodium in the hydroxide.

For the sake of comparison, the analytical results have been arranged in tabular form. The results themselves are averages obtained in duplicate determinations. The weights are given in grms. :—

| Solutions. | No. I. | No. II. | No. III. | No. IV. | No. V. |
|---|---|---|---|---|---|
| Time .. .. .. | 1 h. 30 m. | 2 h. | 2 h. 30 m. | 3 h. 30 m. | 6 h. 40 m. |
| Ampères .. .. | 3·1 | 3·1 | 3·2 | 3 | 3·1 |
| Ampère-hours .. | 4·6 | 6·2 | 8 | 10·5 | 20·7 |
| Na in $Na_2SO_4$.. | 0·0251 | 0·0441 | 0·0563 | 0·0915 | 0·1604 |
| Na in $Na_2S$ .. | 0·1096 | 0·0806 | 0·0515 | 0·0354 | — |
| Na in $Na_2S_2O_3$. | 0·0131 | 0·0158 | 0·0145 | 0·0086 | 0·0019 |
| Na in NaOH .. | 0·0236 | 0·0320 | 0·0492 | 0·0367 | 0·0090 |
| | 0·1714 | 0·1725 | 0·1715 | 0·1722 | 0·1713 |

Barring experimental errors in the preparation of the standard solution subjected to electrolysis and analysis, each should contain 0·1718 grm. of sodium per 50 c.c. It will be seen that the weight of sodium in sodium thiosulphate plus sodium in the hydroxide, sulphate, and sulphides corresponds so closely to the theoretical weight of sodium in 50 c.c. of the solution that it seems impossible to have the oxidation take place through the formation of any compound or compounds of sodium besides those above mentioned. Sulphides disappear first, the hydroxide next, and the thiosulphate last of all.

The method used for the estimation of the polysulphides of sodium is based upon the fact that, when an alkaline solution of zinc chloride is added to a solution of poly-

sulphides, the sulphur above one atom separates out, and zinc sulphide is produced. The free and combined sulphur can then be filtered off, oxidised to sulphuric acid and zinc sulphate by bromine, and calculated from the weight of the barium sulphate which results on addition of hydrochloric acid and barium chloride. The resulting weight of sulphur is that of all the sulphur in sulphides and polysulphides. By subtracting the weight of sulphur that would combine with the weight of sodium, found by means of the standard solution of zinc chloride, to form sodium sulphide, the weight of sulphur in the polysulphides of sodium above one atom has been obtained.

Solutions I., II., III., and IV. gave the following weights (in grms.) of sulphur above one atom in the polysulphides :—

| I. | II. | III. | IV. |
|---|---|---|---|
| 0·0208 | 0·0256 | 0·0415 | 0·0199 |

These determinations are valuable inasmuch as they show the amount of polysulphide present at different stages of the electrolysis, and correspond, as nearly as could be judged, to the varying intensity of the yellow colour in the solutions.

The effect of a 3-ampère current at 50 volts, alternating 130 times per second, was next tried upon three sulphide solutions.

Platinum wire, either double or single, was used for the electrodes. After the electrolysis, the solutions were filtered and diluted with water to 1000 c.c. Theoretically, therefore, 50 c.c. of No. I. contain 0·1716 grm. of sodium ; No. II., 0·1802 grm. ; and No. III., 0·1802 grm. The methods used in the analyses of the solutions obtained by use of the direct current and already described have been used over again in the analysis of I., II., and III., and the results are below. The weights are given in grms.

| Solutions. | No. I. | No. II. | No. III. |
|---|---|---|---|
| Approximate time of electrolysis | 2 h. | 3 h. 30 m. | 5 h. |
| Approximate number of ampères | 3 | 3 | 3 |
| Na in $Na_2SO_4$ .. .. .. .. | 0·0033 | 0·0107 | 0·0218 |
| Na in $Na_2S$ .. .. .. .. .. | 0·1596 | 0·1152 | 0·0857 |
| Na in $Na_2S_2O_3$ .. .. .. .. | 0·0022 | 0·0249 | 0·0368 |
| Na in NaOH .. .. .. .. | 0·0058 | 0·0299 | 0·0361 |
| | 0·1709 | 0·1807 | 0·1804 |

It would appear from these results, therefore, that the oxidation of sodium sulphide to sulphate by means of the alternating current is the same, so far as chemical changes are concerned, as oxidation by the direct current. The rate of oxidation, using platinum wire electrodes, is, of course, much slower with the alternating current than with the direct when large electrodes were used. However, if the electrolysis were continued long enough, there is no reason to suppose that all the sulphide in the electrolyte could not be oxidised to sulphate. In these experiments it was not considered advisable to carry an electrolysis beyond five hours, inasmuch as the platinum electrodes dissolved under the combined influence of the alternating current and electrolyte, which never happened when the direct current was employed. Some idea of the rapidity with which platinum dissolves under the above conditions can be obtained from a platinum determination made in Solution II. ; 100 c.c. gave 0·0216 grm. platinum. At the end of the electrolysis, therefore, the platinum electrodes weighed 0·216 grm. less than at the beginning. Judging from the red colour in the electrolytes and the precipitation of platinum sulphide when acids were added, sodium thioplatinate was produced. This part of the subject, however, needs further investigation.

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**Pure Ether for Narcotising.**—H. Thoms (*Berichte der Pharm. Gesell.*).—Ether, most carefully purified, is not neutral to litmus-paper, but gives a bluish tint to sensitive red litmus-paper.

# THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

IN compliance with an invitation from the Council of the Iron and Steel Institute, I have pleasure in presenting the following account of the introduction of standard methods in the analysis of iron and steel.

In the first place I must point out that the phrase "introduction of standard methods of analysis" is, strictly speaking, a catch word, and that it would perhaps have been better to speak of a unification of analytical results. Adopting the most general standpoint, it may be said that the only important point to be attained is to ensure that analyses of one and the same sample made by different individuals shall agree well together, and give as accurate results as possible ; and further, that it can be considered somewhat a matter of indifference whether this object is attained by the use of similar methods or in any other possible way. Indeed, it will be seen subsequently that considerable objections may be raised against the introduction of standard methods for general use.

That this object is not at the present time attained in many cases is generally known. Nevertheless I shall venture to cite some examples of analytical differences which may not be without interest, inasmuch as the analyses in question were made, not by beginners, but by experienced, and even eminent, analysts.

A chill-roll (Jüptner, *Fortschritte im Eisenhüttenlaboratorium*, 1895, vol. i., p. 3) was examined in two laboratories (A and B), and as quite incredible differences were obtained, a check analysis (C) was made. The results were as follows :—

| | A. | B. | C. |
|---|---|---|---|
| | Per cent. | Per cent. | Per cent. |
| Carbon .. .. .. | 3·50 | 2·785 | 2·767 |
| Silicon .. .. .. | 1·30 | 0·668 | 0·677 |
| Manganese .. .. | 2·40 | trace | 0·050 |

In one and the same steel sample two laboratories found :—

| | A. | B. |
|---|---|---|
| | Per cent. | Per cent. |
| Phosphorus .. .. .. | 0·11 | 0·0870 |
| Arsenic .. .. .. .. | no trace | 0·0387 |
| Total .. .. .. | 0·11 | 0·1257 |

In one and the same laboratory there was found in the same sample of pig iron which was sent for analysis twice under different designations :—

| | Per cent. | Per cent. |
|---|---|---|
| Combined carbon .. .. | 0·91 | 0·617 |
| Graphite .. .. .. .. | 2·67 | 3·033 |
| Total carbon .. .. .. | 3·58 | 3·650 |
| Silicon .. .. .. .. | 2·65 | 1·179 |
| Manganese .. .. .. | 0·088 | 0·105 |
| Phosphorus .. .. .. | 0·355 | 0·394 |

Happily, however, such enormous differences are rarely met with ; but the fact that they can occur at all is undoubtedly a matter for reflection, and renders it a pressing duty to devise a method of obviating such occurrences.

Notwithstanding most careful and frequent repetitions of the analyses, differences are still met with which under some circumstances may be considerable. Thus the investigation of four standard samples by the English, Swedish, and American Committees gave, according to J. W. Langley (*Journal of the American Chemical Society*, 1893, p. 448) the following results :—

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* Read before the Iron and Steel Institute.

| Stand-ard. | Constituents. | English Commisn. | Swedish Commisn. | American Commisn. | Max. Diff. |
|---|---|---|---|---|---|
| | Carbon | 1'414 | 1'450 | 1'440 | 0'036 |
| | Silicon | 0'263 | 0'257 | 0'270 | 0'013 |
| I. | Sulphur | 0'006 | 0'008 | 0'004 | 0'004 |
| | Phosphorus | 0'018 | 0'022 | 0'016 | 0'006 |
| | Manganese | 0'259 | 0'282 | 0'254 | 0'028 |
| | Carbon | 0'816 | 0'840 | 0'807 | 0'033 |
| | Silicon | 0'191 | 0'185 | 0'207 | 0'017 |
| II. | Sulphur | 0'007 | 0'004 | 0'004 | 0'003 |
| | Phosphorus | 0'014 | 0'015 | 0'010 | 0'005 |
| | Manganese | 0'141 | 0'145 | 0'124 | 0'021 |
| | Carbon | 0'476 | 0'500 | 0'452 | 0'048 |
| | Silicon | 0'141 | 0'150 | 0'152 | 0'011 |
| III. | Sulphur | 0'008 | 0'006 | 0'004 | 0'004 |
| | Phosphorus | 0'021 | 0'021 | 0'015 | 0'0c6 |
| | Manganese | 0'145 | 0'170 | 0'140 | 0'030 |
| | Carbon | 0'151 | 0'170 | 0'160 | 0'019 |
| | Silicon | 0'008 | 0'015 | 0'015 | 0'007 |
| IV. | Sulphur | 0'039 | 0'048 | 0'038 | 0'010 |
| | Phosphorus | 0'078 | 0'102 | 0'088 | 0'024 |
| | Manganese | 0'130 | 0'130 | 0'098 | 0'032 |

The examination of the four samples by the chemists of the British Committee gave the following results :—

| Stand-ard. | Constituents. | W. Jen-kins. | G. S. Packer. | J. Pat-tinson. | E. Riley. | J. E. Stead. | Max. Diff. |
|---|---|---|---|---|---|---|---|
| | Carbon | 1'43 | 1'44 | 1'393 | 1'387 | 1'419 | 0'053 |
| | Silicon | 0'260 | 0'28 | 0'271 | 0'250 | 0'252 | 0'030 |
| I. | Sulphur | 0'010 | traces | trace | 0'004 | 0'007 | 0'010 |
| | Phosphorus | 0'02 | 0'017 | 0'019 | 0'017 | 0'016 | 0'004 |
| | Manganese | 0'26 | 0'267 | 0'263 | 0'278 | 0'229 | 0'049 |
| | Carbon | 0'82 | 0'85 | 0'802 | 0'811 | 0'796 | 0'054 |
| | Silicon | 0'200 | 0'197 | 0'182 | 0'192 | 0'186 | 0'018 |
| II. | Sulphur | 0'008 | traces | 0'007 | 0'007 | 0'007 | 0'008 |
| | Phosphorus | 0'02 | 0'012 | 0'012 | 0'012 | 0'012 | 0'008 |
| | Manganese | 0'14 | 0'144 | 0'145 | 0'140 | 0'137 | 0'008 |
| | Carbon | 0'55 | 0'46 | 0'461 | 0'456 | 0'455 | 0'095 |
| | Silicon | 0'144 | 0'14 | 0'140 | 0'153 | 0'130 | 0'023 |
| III. | Sulphur | 0'015 | traces | trace | traces | 0'008 | 0'015 |
| | Phosphorus | 0'02 | 0'022 | 0'022 | 0'016 | 0'024 | 0'008 |
| | Manganese | 0'13 | 0'130 | 0'158 | 0'144 | 0'161 | 0'031 |
| | Carbon | 0'165 | 0'146 | 0'142 | 0'147 | 0'154 | 0'013 |
| | Silicon | 0'008 | 0'008 | 0'009 | 0'008 | 0'009 | 0'001 |
| IV. | Sulphur | 0'040 | 0'036 | 0'040 | 0'041 | 0'040 | 0'005 |
| | Phosphorus | 0'08 | 0'08 | 0'075 | 0'081 | 0'075 | 0'006 |
| | Manganese | 0'13 | 0'130 | 0'130 | 0'124 | 0'137 | 0'013 |

The examination of the fifth standard sample by the English Commission yielded :—

| Constituents. | G. S. Packer. | J. Pat-tinson. | E. Riley. | J. E. Stead. | Max. Diff. |
|---|---|---|---|---|---|
| Combined carbon | 0'055* | 0'034 | 0'036 | 0'035 | 0'021 |
| Silicon | 0'006 | 0'005 | trace | 0'008 | 0'008 |
| Sulphur | 0'030 | 0'030 | 0'023 | 0'036 | 0'013 |
| Phosphorus | 0'040 | 0'041 | 0'041 | 0'042 | 0'002 |
| Manganese | 0'275 | 0'310 | 0'258 | 0'317 | 0'059 |
| Copper | — | — | 0'025 | — | — |

The American Commission published (*Proc. Amer. Soc. of Civil Engineers*, vol. xxi., pp. 59-67) the following

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* The high percentage of carbon reported by Packer is held to be due to the fact that the determination was effected in T. Brown and Co.'s laboratory in Sheffield, in the centre, that is, of a large works, and therefore in an atmosphere in which dust was always present, so that with the greatest care it was not possible to obtain concordant results. This fact indicates the great importance of maintaining a condition that is subsequently dealt with (favourable position of the laboratory).

results of phosphorus determinations in a series of steel samples :—

| Analyst. | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. |
|---|---|---|---|---|---|
| W. P. Barba | 0'041 | 0'015 | 0'095 | 0'091 | 0'041 |
| A. A. Blair | 0'040 | 0'016 | 0'098 | 0'091 | 0'041 |
| T. M. Drown | 0'042 | 0'016 | 0'104 | 0'090 | 0'042 |
| C. B. Dudley | 0'040 | 0'016 | 0'099 | 0'097 | 0'039 |
| P. W. Shimer | 0'041 | 0'017 | 0'098 | 0'096 | 0'039 |
| Maximum difference | 0'002 | 0'002 | 0'009 | 0'007 | 0'003 |

*Remarks.* — Sample No. 3 contained an appreciable quantity of arsenic.

The differences in these analyses are, it is true, incomparably smaller than in the examples previously cited, and for many technical purposes may be disregarded. They are still, however, quite appreciable enough to have a disturbing influence, not only in purely scientific researches, but also in many instances in practice. The analyses are, however, it must not be forgotten, the careful work of special commissions, and not the average results of very busy works laboratories, from which equally careful analyses cannot well, as a rule, be expected, on account of the excess of work, almost all of which has to be disposed of in the shortest possible time.

In saying this I have no intention of decrying the value of ironworks laboratories. On the contrary, I desire to direct your attention to this point in order to show you that it is just these laboratories which at the present time, under the pressure of urgent necessity, have to conduct enormous numbers of analyses, and, besides this, have frequently to leave to others much more of the laboratory work than the chemists engaged there like—it is just these laboratories that do more work, and better work, than can reasonably be expected from them under these conditions.

Even small analytical differences, however, which unfortunately can in no way be regarded as rarities, frequently make themselves felt in an objectionable manner, not only in purely scientific researches, but also in many cases in practice.

Thus, for example, if a given composition or a given limit to the percentages of the various constituents is specified by the purchasers as a condition of acceptance, it is evident that even very small deviations in the analytical results may have disagreeable consequences. An instance that came under my notice will illustrate this. In an engineering works an order was given for boilers, the plates of which were specified not to contain more than 0'020 per cent of sulphur. The plates were supplied by an iron works, and in them 0'014 per cent of sulphur was found by the producer. As the limit of the contract was very short, the engineering works found it necessary to work the plates supplied on the strength of this determination, without waiting for the check-analysis required by the purchaser. The boilers were finished when the second analysis came to hand ; but this yielded 0'034 per cent of sulphur !

Such examples, of which many might be cited, clearly show the urgent necessity of doing something to meet this evil, and the great importance of being able to be perfectly certain of the results yielded by chemical analysis. The result will show, and reference to it may not be out of place here, that more advantages will also accrue than would at first sight be imagined. If, for example, it were made absolutely certain that the limits of error of the determination of sulphur amounted to, say, ±0'005 per cent, it is evident the works in question, in order to satisfy with safety the required conditions, could supply only such plates as were found to contain not more than 0'010 per cent of sulphur. As, however, it is only rarely that an ironworks is in a position to regularly produce a material with so low a percentage of sulphur, the immediate consequence would be that the purchaser would be compelled to raise proportionately the limits fixed for the allowable percentage of sulphur.

In what manner the investigations required for the solution of this problem can be, and will be, of still further practical use in this direction will be shown later.

The necessity of doing something in order to obtain standard—that is, concordant—analytical results has long been recognised, and in consequence endeavours in this direction have been made for many years past.

Thus, at the instigation of Dr. Dudley, in Altoona, Pennsylvania, an American Commission was formed, consisting of Messrs. Metcalf, Rodd, and Hunt of Pittsburgh, Barba and Blair of Philadelphia, Drown of Boston, and Shimer of Easton, with Mr. John W. Langley as President. This Commission, since the Chicago World's Fair, has worked in conjunction with the English Commission, consisting of Professor W. C. Roberts-Austen (President), Sir F. A. Abel, Bart., E. Riley, J. Spiller, G. J. Snelus, W. A. Tilden, and Thomas Turner, and with a Swedish Commission, consisting of Dr. A. Tamm, Professor C. G. Särnström, Dr. P. E. W. Öberg, Professor O. Pettersson, and R. Åkerman as President. Reports of the British Committee were published by the British Association in 1889, 1890, 1891, 1892, and 1893. Again, in Germany, chiefly by the initiative of the *Verein deutscher Eisenhüttenleute*, and of the late Dr. von Reis, a Commission was formed with similar objects, consisting of Messrs. Wolf of Dortmund, Glebsattel of Oberhausen, Corleis, Gerstner, and Salomon of Essen, and Becker of Rothe Erde, near Aix-la-Chapelle. Moreover, a number of eminent chemists have also for some years past been engaged on similar work, and their endeavours have been supported by premiums offered by technical societies.

In technical literature these endeavours are very noticeable. Thus, in the more recent works on iron analysis (Blair, Wedding, &c.), there is a growing attempt to present comparative criticisms of the various methods, and to study more exhaustively their sources of error.

I myself have been occupied with this work for many years past, and shall here merely refer to an article published in the *Oesterreichische Zeitschrift für Berg- und Hüttenwesen* in 1884 on the accuracy of chemical analysis, and to my two larger treatises, "Praktisches Handbuch für Eisenhütten-Chemiker," 1885, and "Fortschritte im Eisenhütten-Laboratorium in den letzten 10 Jahren," 1895-96, in which not only are the causes of errors in analysis discussed generally, but special attention is also given to criticising the various methods.

At the fifth International Congress for the Unification of Methods of Testing, held at Zürich in September, 1895, the proposal was made by Dr. Wedding and myself, based on papers on the subject read by us, that support be afforded to an International Commission to deal with the solution of this problem, and the motion was carried by the Conference.

Turning now to the problem itself, it is evident that its solution must be preceded by an accurate knowledge of the causes that bring about differences in analyses, so that it is first necessary to consider the sources of error in chemical analyses.

Regarded from a general point of view these are—

1. Gross errors in the analysis.
2. Impure reagents.
3. Errors due to the apparatus, &c.
4. Errors due to the operations.
5. Errors due to the analytical methods.
6. Personal errors.
7. Errors due to differences in the calculation of the analyses caused by the values of the atomic weights on which they are based.
8. Want of homogeneity of the sample.

I trust that it will not be out of place to consider a little more closely these various sources of error.

1. Gross errors in the analysis, with which may also be classed confusion of samples, errors in calculation, &c., should obviously never occur. Their occurrence is due to ignorance, want of skill, or carelessness on the part of the analyst, to defective equipment of the laboratory, and to overwork.

What can and must be done to obviate these errors is evident :—Employment of skilled analysts, diminution as far as possible of laboratory work, suitable equipment of the laboratory, and avoidance of overwork. At the same time, it may not be out of place to consider these points more closely, for now and again it is just in this direction that grave errors are committed. The analysis of steel is generally recognised to belong to the most difficult and most ticklish portion of chemical analysis, and should only be entrusted to skilled and reliable analysts. Moreover, it is, too, by no means the only duty of the ironworks' chemist to conduct his analysis according to known recipes, as in a cookery-book. Not only has he frequently to solve problems in which the known methods leave him in the lurch; but it is also under all circumstances his task, his duty indeed, to make as thorough a study as possible of new methods described in the literature of the subject. In this way his knowledge is widened, and the possibility is presented of introducing effective new methods, and of making it clear to himself what differences can arise by the employment of other methods than those he employs. He, however, has also an opportunity of so modifying new methods that they can be applied with distinct advantage to practical use. Anyone who is unable to test an analytical method thoroughly is unfit to be chemist in an ironworks laboratory.

Analytical chemistry, and not least the branches of it dealing with the investigation of iron and steel, has become so extensive and so progressive a science, that any frequent change of staff in ironworks laboratories is as far as possible to be avoided. For this reason the principle occasionally adopted of employing beginners in the metallurgy of iron in the laboratory, and after a time to find places for them in the works themselves, is to be condemned. It is certainly true that it is of considerable use to works officials if they have worked for some time in the works laboratory ; but it must not be forgotten that the works laboratory is provided in the first place to conduct accurate analyses, and if it is also provided in the interest of the works, it is obviously an absolute necessity that the interests of the laboratory should be fully and completely preserved.

That in modern works laboratories a part of the work must be left to unqualified assistants is a matter for regret, which must be ascribed to the fact that an enormous number of analyses have to be got through as rapidly as possible. It is indeed true that there are such assistants who possess all the qualities for enabling them to carry out analytical work, if a skilled chemist is at hand on the one hand to check their work, and on the other to come to their aid in the case of need. Such assistants are, however, very rare, and on the other hand I have seen, in small works laboratories, where unqualified assistants work without supervision, things (such as determining silicon in grey pig-iron weighing the silica *with the graphite*, in determining tungsten in tungsten steel by fusing the silica and tungstic acid with potassium bisulphate, and extracting the fused mass with boiling water, &c.) which render it my duty to advocate most urgently the limiting, as far as possible, the employment of such assistants as these. Moreover, it is a well-known fact that the best and most certain methods, when they are currently used by these assistants, do not yield nearly such accurate results as in the hands of qualified chemists, and that the supervising chemist has constantly to guard against the introduction by the assistant in the course of time of slight carelessness in performing his duties.

(To be continued).

## NOTICES OF BOOKS.

*Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for* 1895. New Haven: Tuttle, Morehouse, and Taylor.

THE Connecticut Agricultural Experimental Station was established as far back as 1877. It analyses manures, cattle-foods, seeds, milk; identifies grasses, weeds, moulds, blights, mildews, useful and injurious insects, and gives information on subjects of Agricultural Science. It seeks to obtain for analysis samples of all the manures sold in Connecticut, and also samples of foods and drinks sold in the State, with reference to adulterations.

From the report of work done we learn that more than 22,500 tons of commercial manures are introduced yearly into the State, at the expense of more than 700,000 dols.

The law relating to the sale of manures makes the seller responsible for affixing a correct label to every package or lot sold or offered, as well as the payment of an analysis fee of 10 dols. for each fertilising ingredient which the manure contains or is alleged to contain.

The constituents whose determination is necessary are generally nitrogen, phosphoric acid, and potash. The fees are usually 10, 20, or 30 dols., according as one, two, or all of these ingredients exist in the manure.

A sealed sample has to be deposited with the Director of the Station by the manufacturer or importer, and a certified statement of composition must be deposited with him. A statement of the percentage of nitrogen, phosphoric acid, and potash, and of their states is required. The percentage of insoluble phosphoric acid may be stated or omitted.

The law of the State requires that every person in the State who sells any commercial manure, of whatever kind or price, must annually report to the Director of the Experimental Station, and on demand shall deliver a sample for analysis. Gypsum is, rather curiously, considered to come under the law as a "commercial fertiliser."

In the scale of values for the chief manurial ingredients we find nitrogen in ammonium salts valued at $18\frac{1}{2}$ cents per lb.; in nitrates, 15; organic nitrogen in fish, blood, and mixed manures, at $16\frac{1}{2}$ cents; in tankage, 16; phosphoric acid soluble in water, 6 cents per lb.; in dry ground fine fish, $5\frac{1}{2}$; in mixed manures insoluble in ammonium citrate, 2 cents; potash as sulphate free from chlorides, $5\frac{1}{4}$, and as muriate, $4\frac{1}{2}$ cents.

Leather, whether in its untreated state, or steamed or roasted, is declared to be of no manurial value. Dried blood is found to be rich in available nitrogen.

Cotton-seed meal during the past season has been found the cheapest source of available nitrogen. It is as rapidly and fully available as the best forms of animal matter.

" Castor pomace " is a good manure, but very poisonous to stock.

Of the 78 brands of special manure tabulated in this report, 19 are below the manufacturers' guarantee in respect of one ingredient, and 10 in respect of two ingredients.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 3, July 20, 1896.

The Perpetual Secretary announces to the Academy the loss which it has sustained in the person of A. Kekulé von Stradonitz, a correspondent of the Chemical Section, who died at Bonn on July 13th, 1896.

**Study of Lanthanum Carbide.**—Henri Moissan.—Lanthanum oxide, mixed with carbon and heated in the electric furnace, readily produces a transparent crystalline carbide of the formula $C_2La$. This carbide is decomposable by water at the ordinary temperature, yielding a mixture of ethylene and of methane accompanied with traces of ethylene (?). The proportion of methane is a little higher than that afforded by cerium carbide. At the moment of its destruction by water this compound furnishes a very small quantity of liquid and solid carbides.

**Electroscope with Three Gold Leaves.**—L. Benoist.—With three leaves the angle of limit extends to 120°. The apparatus may thus serve for higher potentials without fear of the gold leaves being torn off.

**On Metallic Alloys.**—Henri Gautier.—This paper requires the two accompanying figures.

**Oxy-Salts of Mercury.**—Raoul Varet. —The author concludes that the oxy-salts of mercury follow strictly the law of thermo-chemical modules; that mercuric nitrate is in the state of a neutral salt in the midst of its nitric solutions; and that mercuric sulphate dissolved in an excess of sulphuric acid is in a state of an acid salt absolutely comparable to the corresponding potassium and sodium salts.

**Action of Haloid Compounds of Phosphorus upon Iron, Nickel, and Cobalt.**—A. Granger.—The results obtained are—

| | Calculated as $Fe_4P_3$. | Found. |
|---|---|---|
| Iron .. .. .. .. | 70·64 | 71·04 |
| Phosphorus .. .. | 29·36 | 29·44 |

| | Calculated for $Ni_2P$. | Found. |
|---|---|---|
| Nickel .. .. .. | 79·20 | 79·09 |
| Phosphorus .. .. | 21·80 | 20·98 |

| | Calculated for $Co_2P$. | Found. |
|---|---|---|
| Cobalt .. .. .. | 79·20 | 79·61 |
| Phosphorus .. .. | 21·80 | 20·43 |

**Some Combinations of Iodic Acid with other Acids.**—Paul Chretien.—The author has obtained and described the molybdo-iodic salts of sodium, of potassium, ammonium, and barium, and the free molybdo-iodic acid—

$$I_2O_5,2MoO_32H_2O.$$

He has also produced metatungstic-iodic compounds of the general formula $I_2O_5(4WO_3)m\,M_2OnH_2O$. The phosphoiodic acid has the complex composition—

$$P_2O_5,18I_2O_5,4H_2O.$$
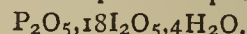
**Action of Ammonia upon Potassium or Sodium Paratungstates.**—L. A. Hallopeau.—The author's observations are a new proof of the dissimilarity existing between the chemical properties of the potassium and sodium paratungstates. The author has already shown that these bodies act in a different manner upon gelatinous zirconia, which dissolves on boiling in potassium paratungstate, but is insoluble in sodium paratungstate.

**Action of Reducing Agents upon the Nitroso-compounds of Osmium.** — L. Brizard. — The amidic chlorosmiate is a reducer. Its solution instantly decolourises permanganate in an acid liquid; in an alkaline liquid there is formed a maroon-brown precipitate. With mercuric chloride there is instantly formed in the cold a grey precipitate, which rapidly blackens. Cupric salts are reduced to the cuprous state.

**Fermentation of Uric Acid by Micro-organisms.**—E. Gerard.—The author's experiments show that certain microbia existing in the air decompose uric acid and form urea.

**Action of Sulphur Chloride upon Pentaerythrite.**—J. Bougault.—This paper is not suited for useful abstraction.

**Determination of the Congelation-point of Dilute Aqueous Solutions.**—A. Ponsot.—Will be inserted in full.

### No. 4, July 29, 1896.

**Certain New Experiments relating to the Preparation of the Diamond.**—Henri Moissan.—A new combustion was made of diamonds prepared in part by means of small cylinders filled with charcoal of sugar, and partly by means of metallic blocks of iron and copper. These two procedures furnished the purest diamonds. They sank in methylene iodide, scratched rubies with ease, and contained no black diamonds. The weight of the diamonds was 5·7 m.grms.; when burnt, they left a trace of ash, the weight of which could not be appreciated with the balance. We collected 20·5 m.m. of carbonic acid. Theory requires for 5·7 m.grms. 20·9 m.m. This substance therefore responds to the fundamental property of carbon, yielding for 1 grm. of substance 3·666 grms. of carbonic acid.

**Study of the Black Diamond.**—Henri Moissan.—We find in nature, both in Brazil and at the Cape, transparent diamonds containing inclosures of various forms. These inclosures may be of different nature, but the most numerous are black, and when abundant afford the variety of crystallised carbon of a fatty aspect which is known by the name of "black diamond." We are able to demonstrate that these black enclosed matters are due to a variety of carbon differing from the diamond in the following respects:—A black diamond of 2·2365 grms., presenting some small flaws, but transparent, was enclosed in a piece of cloth, placed on an anvil, and broken with the hammer. It was split at the first shock, and yielded very distinct pointed octahedra. We reduced the whole to fine powder in an Abich mortar, and this dust, of a blackish grey, is found under the microscope to be formed of fragments. We heat, then, about 1 centigrm. of this powder in a tube of Bohemian glass traversed by a current of oxygen at a temperature lower by 200° than the temperature of combustion of the diamond. The experiment lasts half an hour. We observe very distinctly a slight escape of carbonic acid, which soon ceases, and which is shown by baryta water. After cooling, the diamond has lost its grey tint and has become white. The black matter which was contained in this diamond therefore burns in oxygen, yielding carbonic acid, and the diamond resumes its transparency. The experiment succeeds only with black diamond reduced to a very fine powder.

**Homogeneity of Argon and of Helium.**—W. Ramsay and J. Norman Collie.—(See p. 75).

**Camphoric Mononitrile: its Anhydride and its Anilide.**—A. Haller and M. Minguin.—The authors abandon the further investigation of this subject, as they find that they have to some extent been anticipated by Oddo and Leonardi.

**Mean Density and the Specific Heat of Alloys of Iron and Antimony between 0° and 100°.**—J. Laborde. —The author gives a table showing the quantity of iron contained in the alloys and obtained on analysis, the density of these alloys at 0°, and the specific heat calculated according to the composition. The numbers found for the specific heat are all greater than the numbers calculated according to the rule of mixtures, and the most important differences are much greater than experimental errors. The magnetic properties of these alloys increase abruptly when the proportion of iron reaches and exceeds that corresponding to $Fe_3Sb_4$.

**Study on the Nitrogen and the Argon of Firedamp.**—Th. Schlœsing, jun.—The author has sought for argon in the nitrogen of fire-damp, and has found 1·1 per cent—a proportion very close to that (1·19) which characterises the nitrogen of the atmosphere. He has next sought for argon in the coal of St. Etienne and of Plat-de-Gir, and found that they contain, if any, at most 1/200,000 of an element comparable to argon.

**Cranial Endography by means of the Röntgen Rays.**—MM. Remy and Contremoulins.—The authors have obtained endographic cranial proofs superior in distinctness to any produced hitherto. The superiority of these proofs depends, on the one part, on the use of the arrangement devised by M. Collardeau, and, on the other, to the remoteness of the source of light.

**Preparation of Selenic Acid.**—R. Metzner.—The author uses as his material selenious acid, oxidising it by means of permanganic acid obtained from barium permanganate.

**On a New Cobaltite: Magnesium Cobaltite.**—E. Dufau.—If we heat in the electric arc a suitable mixture of cobalt sesquioxide and of magnesia, oxygen is fixed, and the mixture is completely transformed into crystalline magnesium cobaltite, $CoO_3Mg$.

**Solutions of Trichloracetic Acid.**—Paul Rivals.—A thermo-chemical memoir, not well adapted for abridgment.

**Vinyltrimethylene and Ethylidenetrimethylene.**—G. Gustavson.—The author obtains vinyltrimethylene by causing zinc powder and alcohol to act upon the tetrabromhydrine of pentaerythrite [$C(CH_2Br)_4$]. The combination of vinyltrimethylene with hydriodic acid leads to new substances. The alcohol and the ethyltrimethylene derived from it have been obtained, but not specially studied. I have examined in detail the action of alcoholic potassa upon this iodide. We obtain again a hydrocarbide, $C_5H_8$, but it is an isomer of vinyltrimethylene, boiling at 37·5°. Having regard to the manner of formation of this hydrocarbon, it must be regarded as ethylidenetrimethylene.

**Constitution of Pinacoline.**—Maurice Delacre.—The author distinguishes Butlerow's acetone from pinacoline by the action of aqueous hydrobromic acid. He weighs in each of two stoppered bottles 35 grms. of one and the same concentrated solution of hydrobromic acid, and adds to each, suddenly, and without refrigeration, 10 grms. of the product. With pinacoline the liquid becomes homogeneous, blackish brown, heats, and gives rise in some time to an abundant deposit. With acetone, the mixture remains of a straw yellow, and even after eight days remains perfectly limpid without the slightest deposit.

**Crystallographic Properties of some Alcoyl-camphors of the Aromatic Series.**—J. Minguin.—This paper does not admit of useful abridgment.

**Formation and Etherification of Crotonylic Alcohol.**—E. Charon.—The author accentuates the curious fact that in the reduction of crotonic aldehyd the reaction considered as secondary, and yielding a pinacone, becomes the principal reaction with a yield of 60 per cent.

**Electrolysis of Fatty Acids.**—J. Hamonet.—The author has studied the electrolysis of potassium butyrate and isobutyrate.

# THE CHEMICAL NEWS.

## NITROGEN AND ARGON IN FIRE-DAMP, AND IN THE ROCHEBELLE GAS.

### By TH. SCHLŒSING, Jun.

WE have seen (*Comptes Rendus*, July 27, 1896) by what considerations I have been led to determine exactly the argon contained in the nitrogen extracted from fire-damp, and how I have proceeded in this determination. The following table summarises the principal conditions and the results of these experiments :—

| | Pressure over which the fire-damp is evolved in c.c. of water. | Fire-damp having yielded N with argon. | N with argon extracted from fire-damp. | Argon. | N with argon in 100 of fire-damp. | Argon in 100 of fire-damp. | Argon in 100 N and fire-damp. |
|---|---|---|---|---|---|---|---|
| | C.m. | Litres. | C.c. | C.c. | A. | B. | C. |
| Anzin .. | 400 | 3·5 | 634·0 | 20·78 | 18·1 | 0·594 | 3·28 |
| Bessèges .. | 4 to 5 | 4·9 | 186·7 | 3·04 | 3·8 | 0·064 | 1·63 |
| Firming .. | 16 | 18·4 | 135·8 | 2·27 | 0·74 | 0·012 | 1·67 |
| Liéven .. | 70 | 5·5 | 437·1 | 9·71 | 8·0 | 0·166 | 2·22 |
| Plat-de-Gier | 75 | 1·9 | 592·9 | 10·85 | 30·0 | 0·601 | 1·83 |
| Ronchamp . | 8 | 9·1 | 255·4 | 2·79 | 2·8 | 0·031 | 1·09 |
| St. Etienne | 600 | 15·5 | 497·5 | 5·81 | 3·2 | 0·037 | 1·17 |

The various samples had been taken without the accidental introduction of air. Before analysis I found, by means of phosphorus, that they were absolutely free from oxygen; an insignificant quantity of air introduced into the fire-damp was immediately seized by this reagent.

It is evident how laborious these analyses have been, especially when the fire-damp is very poor in nitrogen; in particular in the study of the fire-damp of Firming, which contains only 0·74 per cent of N. It was requisite to burn 18·4 litres (at 0° and 760 m.m.) of the gas obtained in order to obtain 135·8 c.c. of N, and ultimately 2·27 c.c. of argon. In spite of the material difficulties of the experiments the desirable precision was, I believe, realised. I give as a proof the following verifications. On two samples, which had led respectively to the smallest and the greatest value of the proportions of argon per cent of nitrogen and argon, I repeated the entire series of operations, and obtained :—

| | Vols. at 0° and 760 m.m., fire-damp having yielded N with argon. | N with argon extracted from fire-damp. | Argon. | Argon in 100 N and argon. | Difference. |
|---|---|---|---|---|---|
| | Litres. | C.c. | C.c. | | |
| Ronchamp— | | | | | |
| 1st determ. | 9·1 | 255·4 | 2·788 | 1·092 } | 0·006 |
| 2nd determ. | 7·8 | 218·2 | 2·369 | 1·086 } | =1/180 |
| Anzin— | | | | | |
| 1st determ. | 3·5 | 634·0 | 20·779 | 3 277 } | 0·013 |
| 2nd determ. | 2·0 | 360·0 | 11·752 | 3·264 } | =1/250 |

We have thus arrived the second time at the same results as the former within about 1/200, and this with samples of fire damp in which the argon forms only 1/170 or merely 1/3300. Argon, in virtue of its chemical inertia, can be determined (as we see) with a rare accuracy. Experimentalists should take every opportunity of taking up its determination, which cannot fail to be sometimes highly instructive, instead of restricting themselves to qualitative recognitions.

I will add the figures yielded by another gas, obtained also from coal-beds, but quite different from fire-damp in its constitution. I speak of the gas evolved in the mines of Rochebelle with such dangerous force and suddenness, and which consists essentially, as is known, of carbonic acid. I have been able to make a complete analysis of it, from which results the following centesimal composition : — $CO_2$, 98·13 ; N (and argon), 1·14 ; $CH_4$, 0·73. The nature of the hydrocarbon here mentioned has been established with the eudiometer with perfect distinctness. I have also sought for argon in the gas of Rochebelle, and have found—

| Vols. at 0° and 760 m.m. Gas of Rochebelle treated. | N with argon extracted. | Argon. | N with argon in 100 of the gas treated. | Argon in 100 of the gas treated. | Argon in 100 of N and argon. |
|---|---|---|---|---|---|
| Litres. | C.c. | C.c. | | | |
| 20·0 | 228·9 | 4·29 | 1·14 | 0·021 | 1·87 |

These results lead to various conclusions.

The argon, the presence of which I have shown in fire-damp, has been found in all the samples where I have sought for it. It exists also in the gas of Rochebelle. I have made the spectral verification in three samples from Anzin, Plat-de-Gier, and St. Etienne.

The percentage of nitrogen in fire-damp (column A) varies in the ratio of. 1 : 40 ; in that of argon (column B) as 1 : 50. Nitrogen and argon are therefore met with in proportion which seem to have no relation with that of methane, the principal gaseous product derived from the materials of coal. This is an additional reason for placing the origin of the two gases outside the decomposition of these materials.

Whilst the nitrogen and the argon contained in 100 parts of fire-damp have undergone such wide oscillations, they have varied with reference to each other (column C) only in the proportion of 1 : 3 ; they seem in some manner connected together.

The percentage of 1·17 argon (or 1·18 after correction) in 100 nitrogen and argon, a proportion which characterises atmospheric nitrogen (1 : 19) which is found in the specimens from St. Etienne, examined the first in date, and whence was derived the idea of *fossil air* imprisoned for a long time in the coal, no longer presented itself in the sequel.

It is possible that the air has intervened otherwise, in a less direct manner, in the composition of fire-damp. It may have been introduced into this gas with the concurrence of water. Water saturated with air may have been able under certain conditions to give up to the fire-damp the gases which it held in solution. We should thus explain to ourselves that in fire-damp the percentage of argon in the mixture of nitrogen and argon rose above 1·19, a figure corresponding to the nitrogen of the air; for in the two gases dissolved in water the proportion is now 2·8, and in particular conditions it may reach 3·28. It would, in any case, seem very natural that water, which plays so great a part in the history of coal, should effect exchanges of gas with fire-damp. It would thus form that link, certainly very supple, the existence of which we trace between nitrogen and argon.

Further, the argon of fire-damp is not of necessity derived from the air. What is the source of argon on our globe ? We do not know. Perhaps there exist in the depths reserves capable of diffusing it around them. It is known that Bouchard and Troost have found it along with helium in the mineral waters of Cauterets. Then Ch. Moureu has detected it, also with helium, in the waters of Maizières (*Comptes Rendus*, cxxi., p. 819). Thus argon seems generally diffused in the subterranean regions, as it is in our atmosphere. From this point of view the determinations of argon in the various gases escaping from the earth may yield verification of a high interest.

Whatever is the value of these hypotheses, there remain facts well established by the experiments above described: the presence of argon in fire-damp and in the gas of Rochebelle. There remain precise numerical determinations which may perhaps be of service to geologists.—*Comptes Rendus,* cxxiii., p. 302.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

*To* MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
*Water Examiner, Metropolis Water Act,* 1871.

London, August 11th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined by us all but one were found to be clear, bright, and well filtered.

There is again a serious deficiency in the amount of rain that should, according to the thirty years average, have fallen in the Thames Valley during the past month.

The average fall is .. ..    2·68 inches
The actual fall at Oxford..    1·40   „

Deficiency .. ..    1·28   „

This makes the deficiency of rainfall to the end of July 5·66 inches.

The rainfall has been very unevenly distributed throughout the month; of the 1·40 inches measured, 0·82 in. fell on the 7th, the remainder, 0·58 in., being distributed over ten separate days.

Our bacteriological examinations give the following results:—

|  | | Colonies per c.c. |
|---|---|---|
| Thames water, unfiltered .. .. .. .. .. | | 2731 |
| Thames water, from the clear water wells of the five Thames-derived supplies.. | highest | 46 |
| Ditto ditto .. .. .. .. | lowest | 6 |
| Ditto ditto .. (12 samples) | mean | 21 |
| New River water, unfiltered .. .. .. .. | | 1886 |
| New River water, from the Company's clear water well .. .. .. .. .. .. | | 22 |
| River Lea water, unfiltered .. .. .. .. | | 2859 |
| River Lea water from the East London Company's clear water well .. .. .. .. .. | | 33 |

These results, like those of the chemical analyses given in the Tables, show that the quality of the water now being supplied to London is perfectly wholesome and of excellent quality.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

## CONTRIBUTIONS TO THE STUDY OF THE ANALYTICAL CHARACTERS OF THE COMPOUNDS OF TUNGSTEN.

By E. DEFACQZ.

ON resuming the study of some compounds of tungsten, and having need of a sensitive reaction to show the presence of tungstic acid, I have been led to take up the analytical study of the compounds of tungsten, and I am about to summarise this study.

We know that all the compounds of tungsten may be transformed either into tungstic acid or into an alkaline tungstate. It is also known that we may obtain an alkaline tungstate by fusing the metallic tungstates, soluble or insoluble, with an alkaline carbonate. The alkaline tungstates thus obtained are very numerous; certain of them undergo various transformations on dissolving them in water and submitting these solutions to prolonged ebullition.

Reagents give, with the solutions of different varieties of tungstates, precipitates whose physical characters and composition depend not only on the variety of the tungstate, but also on the conditions of temperature and solution in which the precipitation has been effected. There exists, however, a character common to all the varieties of tungsten by which we can recognise the presence of tungstic acid — the blue colouration obtained on adding to the dilute solution of an alkaline tungstate a fragment of zinc or of aluminium, and some drops of hydrochloric, sulphuric, or phosphoric acid. This reaction is not extremely sensitive.

Lucien Lévy has indicated the colouration due to the action of titanic acid upon some sulphuric solutions of phenols and of alkaloids; we have thought that tungstic acid might produce similar reactions.

The compound of tungsten is at first converted into tungstic acid; in most cases we may take the dry substance under analysis. We then treat this acid with four or five times its weight of potassium bisulphate and some drops of sulphuric acid, and heat gently. Under these conditions the tungstic acid dissolves. We then add so much sulphuric acid that the contents of the capsule do not solidify on cooling. We take a drop of this sulphuric solution, and add a drop of the reagent if liquid, or a few particles if it is solid; triturate for a few instants with the end of a stirring-rod, when we obtain colourations sometimes of an extreme intensity. We have tried the action of numerous organic bodies (carbides, alcohols, ethers, aldehyds, acetones, amines, phenols, alkaloids, &c.). The phenols and the alkaloids have given the best results.

On operating upon a drop of the sulphuric solution, as described above, we obtain with—

|  | Colouration. |
|---|---|
| Phenol .. .. .. .. | Very intense Saturn red. |
| Paracresol .. .. .. | Intense red-brown. |
| Thymol .. .. .. .. | Vermilion. |
| Hydroquinone .. .. | Very intense amethyst-violet. |
| Resorcin .. .. .. .. | Red-brown. |
| Pyrocatechine .. .. | Black-violet, sometimes black. |
| Pyrogallol .. .. .. | Red-black. |
| Naphthol (α) .. .. .. | Violet-blue. |
| „ (β) .. .. .. | „ |
| Salicylic acid.. .. .. | Very intense Saturn red. |
| Oxybenzoic acid (meta) | Feeble Saturn red. |
| „ „ (para) | Nothing. |
| Quinine .. .. .. .. | Slight yellow. |
| Cinchonine .. .. .. | „ |
| Morphine .. .. .. | Amethyst-violet, then brown. |
| Codeine .. .. .. .. | Rose, turning violet. |
| Conicine.. .. .. .. | Intense rose. |
| Solanine.. .. .. .. | Gamboge. |
| Veratrine .. .. .. | Intense sienna, then red-brown. |
| Aconitine .. .. .. | Yellowish brown. |
| Narceine .. .. .. | Yellowish green, then moss-green. |
| Picrotoxine .. .. .. | Orange-red, very intense. |

In general these colourations are destroyed by water.

Strychnine, brucine, nicotine, atropine, cantharidine, caffeine, santonine, pilocarpine, ergotinine, and hyoscyamine give no colouration.

Among these reactions we retain only the colourations given by phenol (red) and hydroquinone (violet), both from their intensity and the ease of procuring the reagent. These colourations easily detect the presence of $\frac{1}{100}$ to $\frac{1}{500}$ m.grm. of tungstic acid. — *Comptes Rendus,* cxxiii., No. 5.

## THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.[*]

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

(Continued from p. 83).

IT is obvious that the size and equipment of the laboratory must fulfil the given requirements. I can therefore confine myself to a few points which now and again are not sufficiently regarded.

The laboratory must be of sufficient size to utilise satisfactorily the working efficiency of those engaged in it, and to avoid confusion. The balance must be in a separate place. The situation of the laboratory should be so chosen that it suffers as little as possible from dust and vibration. It should therefore be placed neither immediately next to the street, nor too close to the works. It is decidedly open to objection to have a laboratory in a works, and the slight advantage thereby presented of convenient access from one to the other is not nearly enough to compensate for the drawback that in such a laboratory accurate results can never be obtained with certainty.[†]

For hygienic reasons the height of the laboratory should not be less than 13 feet, and perfect ventilation is requisite. Central heating of the laboratory is very desirable, more especially because the dust caused in the lighting and emptying of the stove is avoided. Gas is almost indispensable, and can, where coal-gas is unavailable, be easily supplied by a small oil-gas plant. I may also mention that the amount of work done in a laboratory is increased if there is no break in the middle of the day, the work being carried on continuously, and finished at a correspondingly earlier period. In this way opportunity is afforded the staff of obtaining free time for the relaxation so necessary after arduous laboratory work.

It is hardly necessary to state that overwhelming the laboratory with work should be avoided if trustworthy work is anticipated. A laboratory working like a factory is preposterous. And yet in this respect many are to blame. How is it possible to avoid errors and faults with excess of work in many cases almost inconceivable ?

The demands here set forth in the interest of the laboratories (but also in that of the iron industry) will perhaps appear to many as exaggerated. If, however, it is desired to obtain really good and trustworthy analyses, they are not overstated at all. On the contrary, they are the indispensable preliminary conditions which, if unfulfilled, result in all subsequent work having but little value. Nevertheless, it can and will be replied that in all cases such painful accuracy is not required, and how can small works soar to the heights of the required installations ?

Here, however, it is merely a question of alternatives.

In many cases the greatest possible accuracy is indispensable, and without it there is no certain agreement between the investigations of different laboratories. Where, however, it is desirable to have accuracy and agreement with other analysts (and this is very frequently the case), the technical laboratory of an iron-works is a scientific establishment, and must be suitably provided as regards staff, space, time, and equipment.

Undoubtedly there are many investigations (especially the daily analysis for checking the working) in which such minute accuracy is not absolutely necessary, and for such purposes the demands may be considerably modified. If this is done, it must be clearly understood that it is no longer a question of a *chemical laboratory,* but of an *assay office,* and that the determinations thus obtained are not, as a rule, comparable with the results of actual chemical analyses. Where, too, chemical laboratories and assay offices are under the same direction, it is advisable to place them in distinct buildings, and not to employ the staff simultaneously in the two.

In this way it is possible to meet the requirements cited above. Any works, even the smallest, can have its assay office, if one of the managers will only give himself the trouble of superintending the work in it. Larger works, however, can and should have their own actual chemical laboratory, provided with a suitable staff and equipment. The comparatively small expense will certainly be well repaid. But small works, which are not in a position to provide and to maintain their own well-equipped laboratory, do best to have recourse to a neighbouring private laboratory of repute. In that way they fare better and cheaper than with a badly equipped laboratory of their own, which costs, it is true, very little, but which, from the inaccuracy of the work done, does more harm than good.

2. *The want of purity of the chemical reagents* is, as Dr. H. Wedding rightly remarked in his paper at the Zurich Congress, "most easily corrected by care on the part of the chemist *before* using the reagents." By paying careful attention to this point, very advantageous pressure will incidentally be brought to bear on those manufactories which produce reagents on a large scale. Nevertheless, testing the purity of the reagents is not always so simple as many imagine, and this, C. B. Dudley (*Journal of Analytical and Applied Chemistry,* 1893, p. 5), for example, has clearly proved when he says that, as a rule, blank trials are better than the purity tests, as an investigation of the reagents is often accompanied by most difficult manipulations, and it does not of itself clearly show how the impurities will affect the analysis.

3. *Errors due to the apparatus* include all errors in weighing and measuring, errors which are caused by neglecting to reduce weights and volumes to vacuum or to normal pressure and temperature, &c. Although these errors are more or less recognised, and are in many cases so small that they may be neglected, I venture at least to refer to them briefly, as every analyst has to assure himself as to their magnitude in order to be able to allow for them in cases where it appears to be necessary.

*a. Errors in Weighing.*—It is obvious that the balance employed should not be too sensitive nor too sluggish, and that the sensitiveness of the balance (a very important point in steel analysis) should be as nearly as possible constant with loads of various weights. On the other hand, the most perfect equality of the arms of the balance is not absolutely necessary, as both the substances to be weighed and the weights are always placed on the same side of the balance, and *absolute* accuracy of the weighing is in no way desired, as even in important determinations of percentage composition relative accuracy of the weighings perfectly suffices. This circumstance necessitates, however, that, at any rate in all cases in which considerable accuracy is required, all the weighings for *one* analysis must be performed on the same balance.

It is important that the terminal knife edges of the beam should be parallel to each other and to the central knife edge, as otherwise an accurate weighing is quite impossible. Thus, for example, with a balance made by an eminent firm, in which this condition was not fulfilled, two weighings of a small platinum crucible immediately fol-

lowing one another gave a difference of 0·007 grm. (Juptner, "Praktisches Handbuch für Eisenhütten-Chemiker," p. 83).

Accuracy of the weights is similarly urgently required for obtaining correct weighings, but in this case, for the reasons previously given, relative accuracy suffices. In order to effect this a comparison of the separate weights is indispensable. Further, a testing of the graduation of the beam is not to be neglected.

In the course of time the weights, however, suffer changes, which, according to a Report of the German Commission (*Chemiker Zeitung*, x., p. 1481), may be ascribed mainly to the following causes :—

1. *Wear.*—As a rule, the wear is less in proportion to the smoothness of the surface, and therefore highly-polished weights are to be preferred to those with a dull surface.

2. Accumulation of foreign matter on the surface of the weights.

3. *Internal Oxidation.*—This takes place within the blowholes in the castings, and is considerably assisted by the penetration of salt solutions in the galvanic gilding or nickel plating. The weights, therefore, after the receiving of a galvanic deposit, should be repeatedly boiled in water, in order to remove the penetrated salt solution. Old weights that have become inaccurate by internal oxidation should, after re-adjustment, not be again gilded. Very small weights may advantageously be made, not of cast-brass, but of pieces of copper which have been obtained from a piece of electro-deposited copper, or from metal rendered compact by rolling and hammering.

The balance also suffers similar changes to the weights. Besides these permanent changes, however, there are temporary changes, which may briefly be discussed.

The length of the balance-beam may be changed unequally by heating. The weighing of warm substances should therefore be avoided, and care should be taken to avoid any one-sided heating of the balance, whether it be from a gas or petroleum lamp placed nearer to one beam than to the other, or whether it be merely from sunlight reflected from a window-pane. For this reason, as well as a protection from disturbing currents of air caused by breathing, weighings should be conducted only with closed balances. The balances made by A. Ruepprecht, Vienna, in which all the weights under 1 grm. can be placed in position with the case closed, are for these reasons deserving of much commendation.

According to R. Hennig (*Zeitschrift für Instrumentenkunde.* v., p. 16) air currents may also be induced when liquids are weighed in wide vessels owing to their evaporation, which may result in an alteration of the point at which the balance comes to rest. An error in weighing, which amounted to 0·4 m.grm., resulted in one such instance, and this could only be eliminated by determining the zero point of the balance immediately after the weighing, and without removing the liquid from the balance case. The presence of a substance which will absorb the vapour increases the error, such as calcium chloride or sulphuric acid in the case of moisture. The zero point of the balance may, too, be changed by an electrification of the balance supports, after rubbing one side with a cloth, or by frequent lightly-applied friction, such as moving backwards and forwards a box of weights on the cover of the balance case. Similar errors may also be induced, according to the observation of the German Commission (*Chem. Zeit.*, xii., 494), in removing glass or quartz weights from the box by their rubbing against the cloth lining, and so becoming electrically charged.

The condensation of moisture, or even it may be the accumulation of a denser gas layer on the surface of dry non-hygroscopic bodies, induces further errors in weighing, especially in the weighing of U-tubes, &c. Thus G. Papasogli (*L'Orosi*, x., p. 109; *Chemisches Centralblatt*, xvii., p. 559; Fresenius, *Zeitsch. f. Anal. Chem.*, 1888, p.

642) found that various powdered substances, which had been dried over sulphuric acid, increased in weight during the period of weighing (from three to six minutes) by from 0·001 to 0·003 grm.

When closed vessels are to be weighed, care must also be taken that the air enclosed in them has the same temperature and pressure as the surrounding atmosphere.

It has further been shown by T. E. Thorpe (*Journ. Chem. Soc.*, xlvii., p. 116) that the zero point of the balance is subject daily to slight variations, just as if one arm of the balance expanded somewhat more during the course of the day than the other.

β. *Errors in Measuring.*—It is of course evident that the various measuring vessels must be examined as to the correctness of their division and their relative agreement with each other. As a rule, an error of 0·1 per cent of the volume to be measured may in such cases be tolerated, although in especially important cases it will be necessary to take into calculation the exact volumes, for which reason it is advisable to provide correction tables for the measuring vessels that are used.

In reading off the volumes errors may also be made—errors in reading off—which may in part be parallax errors, and in part be due to errors made in estimating portions of the divisions into which the measuring vessel is subdivided. Various methods have been proposed for diminishing the first of these errors (mirrors, floats, &c.). With the necessary practice the parts of one subdivision of the measuring vessel may be estimated to within about one-tenth of a division (the error is about ± 0·1), and in all cases it may easily be estimated to within a quarter of a division.

Other errors result from the adhesion of the liquids to the sides of the vessel, and also in the way they are allowed to flow out, the mere reference to which will suffice.

γ. *Omitting to take into Consideration the Reduction of the Weights to Vacuo.* — According to the principle of Archimedes, every body which is plunged into a liquid or gaseous body loses so much of its weight as is equivalent to the weight of the body it displaces. This naturally leads to errors in the results of weighings ; and although in many cases these are so slight that they need not be considered, yet occasionally they reach such an important amount that it appears desirable to take them into consideration.

For ordinary atmospheric conditions (height of barometer, temperature, degree of humidity), for the reduction of the weights to *vacuo*, the following formula holds good :—

$$P = p \left[ 1 + 0\cdot0012 \left( \tfrac{1}{s} - 0\cdot12 \right) \right],$$

in which P is the weight *in vacuo*, $p$ the weight on the balance, and $s$ the specific gravity of the body to be weighed. It is assumed in this that the weights were of brass (sp. gr. 8·4).

Some examples may serve to show the differences between the weights in air and *in vacuo* :—

For ignited ferric oxide (sp. gr. 5·12) the formula shows $P = p (1 + 0\cdot000096)$, that is to say, a difference in weight of about 0·01 per cent; for alumina, which has been heated to redness, with a sp. gr. of 3·85, the formula yields $P = p (1 + 0\cdot000168)$, a difference in weight of 0·017 per cent ; for magnesium pyrophosphate (sp. gr. 2·40, $P = p (1 + 0\cdot00036)$, or a difference of 0·036 per cent ; and finally, in the case of silica, sp. gr. 2·20, $P = p (1 + 0\cdot000396)$, that is to say, a difference of about 0·040 per cent.

While, then, in almost every case no correction need be made for ferric oxide and alumina, in the two last cases mentioned under certain conditions somewhat important differences may result, as, for instance, about 0·01 per cent in the analysis of magnesite, of 0·036 per cent for calcined magnesite, and of 0·006 per cent in the analysis of a ferro-silicon with 14 per cent of silicon.

If platinum weights are used for the weighing, as is usually the case with the small quantities of substances

commonly used for analysis, the differences become somewhat larger. The reduction formula is then—

$$P = p \left[ 1 + 0 \cdot 0012 \left( \tfrac{1}{5} - 0 \cdot 05 \right) \right],$$

and one obtains therefore, in the cases above given, the following results:—Ferric oxide, $P = p \, (1 + 0 \cdot 00018)$—difference in weight = $0 \cdot 018$ per cent; alumina, $P = p \, (1 + 0 \cdot 00025)$ — difference in weight = $0 \cdot 025$ per cent—magnesium pyrophosphate, $P = p \, (1 + 0 \cdot 00044)$—difference in weight = $0 \cdot 044$ per cent; silica, $P = p \, (1 + 0 \cdot 00048$—difference in weight = $0 \cdot 048$ per cent. The analysis differences are consequently as follows :—In the case of magnesite $\Delta = 0 \cdot 013$ per cent; with calcined magnesite, $0 \cdot 044$; and with 14 per cent ferro-silicon, $0 \cdot 007$ per cent.

The errors induced by this are, it is true, not very important, but they deserve to be considered in accurate work, especially in the presence of other sources of error which are similar in their effects, such, for instance, as the very marked solubility of magnesium pyrophosphate.

These conditions must, however, also be considered from another point of view. As a rule, the weights used for quantities exceeding 1 grm. are of brass, but of platinum for fractions of a grm., and finally the riders are made of aluminium. If these weights are entirely concordant in air, this is not true of their weights as reduced to *vacuo*. As a rule, the weighings of the original substance, if they exceed 1 grm., are, however, made with brass weights, but in the subsequent weighings of the much smaller quantities to be dealt with during the course of the analysis platinum weights are employed. The result is that the total weight of the several constituents can never agree exactly with the weight originally taken for the analysis, which in reality it ought to do.

(To be continued).

## NOTES ON THE
## ELECTROLYTIC DETERMINATION OF IRON, NICKEL, AND ZINC.

By H. H. NICHOLSON and S. AVERY.

THE experimental part of this work was undertaken in the spring of 1892. During the progress of the work various articles on the electrolytic deportment of these metals have been published. Some of these investigations are closely related to those carried out by us. As, however, they differ in some important particulars, and as some observations have been made which, so far as we are aware, have not as yet been reported, it seemed well to present the results obtained although some parts of the work are still incomplete.

In the method of manipulation, free use was made of the text-books of Classen and Smith. A number of cells of the Grove-Tyndall form furnished the current. The current was controlled by means of a rheostat-box. The ampèrage was determined by means of a "Weston" volt-meter. The metals were deposited in platinum dishes of 300 c.c. capacity.

In no case was any attempt made to separate metals by careful regulation of the voltage, as the practical utility of such methods may be doubted till the literature of the subject is more copious.

### I.—*The Electrolytic Deportment of Iron.*

The method of Classen and V. Reiss (*Ber. d. Chem. Ges.*, xiv., 1622) for the determination of the metals in their double oxalate solutions, a method which gives such admirable results in most determinations, cannot be applied with the same degree of convenience to iron, as a strong current and a hot solution are necessary.

Smith and Muir (*J. Anal. Chem.*, v., 488) found that iron is very readily precipitated from ammonium tartrate solutions containing free ammonia. They found, however, that under such circumstances the iron contains carbon. Still tartrate solutions seemed to offer possibilities for quantitative determinations sufficient to warrant a fuller investigation of the subject.

Six grms. of tartaric acid were dissolved in water and added to a solution of ferrous sulphate. The solution was then diluted to 150 c.c. and rendered strongly alkaline with ammonia. The solution was then placed in a platinum dish, submitted to the action of a current of $0 \cdot 115$ ampère and 4 volts for six hours.

Taken, $0 \cdot 0477$ grm. iron. Weight found, $0 \cdot 0476$ grm. iron.

After weighing, the precipitate was dissolved in dilute sulphuric acid. A trace of the odour of hydrocarbons was present. The solution was then oxidised, precipitated with ammonia, and determined in the usual gravimetric way. The weight of the iron oxide corresponded to $0 \cdot 0465$ grm. of iron. The carbon present evidently compensated for the weight of the unprecipitated iron.

The following determinations were made in a similar manner :—

| No. | Current. Ampère. | Time. Hours. | Solution. | Iron taken. Grm. | Weight found. Grm. | Carbon by difference. Grm. |
|---|---|---|---|---|---|---|
| 1. | $0 \cdot 185$ | 4 | Strongly alkaline. | $0 \cdot 0620$ | $0 \cdot 0418$ | — |
| 2. | $0 \cdot 115$ | 14 | Strongly alkaline. | $0 \cdot 0476$ | $0 \cdot 0487$ | $0 \cdot 0011$ |
| 3. | $0 \cdot 115$ | 6 | Slightly alkaline. | $0 \cdot 0291$ | $0 \cdot 0294$ | $0 \cdot 0003$ |
| 4. | $0 \cdot 5$ | 5 | Strongly alkaline. | $0 \cdot 0476$ | $0 \cdot 0492$ | $0 \cdot 0018$ |
| 5. | $0 \cdot 5$ | 5 | Strongly alkaline. | $0 \cdot 0351$ | $0 \cdot 0364$ | $0 \cdot 0013$ |

These figures show that strong currents and free ammonia are favourable to the precipitation of carbon. Hence attention was turned to the electrolysis of iron in neutral ammonium tartrate solutions.

To 25 c.c. of an iron sulphate solution, sodium hydroxide was added till the greater part of the iron was precipitated. A dilute solution of tartaric acid was now added till the greater part of the precipitate was dissolved; 5 grms. of ammonium tartrate were added and the whole diluted to 150 c.c. The solution made up in this way was found to be exactly neutral to litmus. It was necessary to employ a stronger current than when free ammonia was present. The following determinations were made :—

| No. | Current. Ampère. | Time. Hours. | Iron taken. Grm. | Weight found. Grm. | Iron calculated from $Fe_2O_3$. Grm. |
|---|---|---|---|---|---|
| 1. | $0 \cdot 4$ | 6 | $0 \cdot 0630$ | $0 \cdot 0634$ | — |
| 2. | $0 \cdot 4$ | 6 | $0 \cdot 0630$ | $0 \cdot 0635$ | — |
| 3. | $0 \cdot 5$ | $4\tfrac{1}{4}$ | $0 \cdot 0630$ | $0 \cdot 0626$ | $0 \cdot 0620$ |

In all cases carbon was detected in the precipitated iron.

Attention was next given to the determinations of iron in sodium tartrate solutions. In some cases free sodium hydroxide was present. The sodium salt conducts the current much better than the ammonium salt. The precipitation of iron proceeds satisfactorily for a time. After a little black spots appear. When a strong current is employed, a white precipitate of ferrous carbonate forms on the deposited metal. Currents of 2 to 4 volts and of $0 \cdot 05$ to $0 \cdot 1$ ampère were employed to effect the separation of the iron from the solution. Towards the end of the precipitation carbon deposits rapidly. Vortmann (*Chem. Centrbl.*, 1893, 1070), by using currents of low voltage and precipitating the iron in fractions on weighed electrodes, seems to have avoided some of the unfavourable conditions above described. However, the general deportment of iron in sodium tartrate solutions was so unpromising that the investigation was not carried further in this direction.

The question now presented itself :—" Is the precipitation of carbon with iron peculiar to tartrates, or may we expect it when other organic compounds are present?"

To answer this question, a number of qualitative tests were made by adding to the iron solution, before passing the current, solutions of sugar, alcohol, glycerol, or of

salts of formic, acetic, lactic, citric, succinic, or benzoic acids. The currents employed were of the lowest voltage and ampèrage sufficient to give a deposit of several m.grms. in the course of an hour. As ammonium oxalate gives no precipitate of carbon under any circumstances, so far as we are aware, this reagent was used to hold the iron in solution when necessary. The iron was used in the form of ferrous sulphate.

When formates were present in the absence of other organic compounds, no trace of carbon could be detected in the precipitated iron. In all other cases the precipitated iron contained carbon. In the case of citric acid a quantitative determination was made.

A solution of ferrous sulphate containing 5 grms. of citric acid in the form of sodium and potassium salts with a little free acid was submitted for fourteen hours to a current of 0·2 ampère.

Taken, 0·0726 grm. iron. Weight found, 0·0740 grm. iron.

The absence of carbon in the case of oxalates and formates is explained by the fact that these compounds break up under the influence of the current, giving off all carbon, in the form of its highest oxidation product, i.e., carbon dioxide.

In all cases the amount of carbon deposited was increased by the employment of stronger currents, but in no case was it possible to obtain a precipitate free from carbon, except in the case of formates and oxalates, when organic matter was present.

#### Determination of Iron in Solutions containing Ammonium Oxalate and Sodium Borate.

We found that a slight modification of Classen's method greatly facilitated the precipitation of iron. The following gave satisfactory results :—

Twenty-five c.c. of a solution of ferrous sulphate were taken, 5 grms. of ammonium oxalate were added and brought into solution by the aid of gentle heat. Five c.c. of a saturated solution of borax were now added, and the entire solution diluted to 150 c.c. A current of 0·02 ampère was allowed to act on the cold solution for sixteen hours. Towards the end of the operation the anode became covered with a slight brown coating. A slight brown deposit also appeared on the dish above the iron deposit. The following method was used to dissolve these deposits :—Water was added until the surface of the liquid was raised above the brown deposit in the dish. The positive electrode was then brought in contact for a moment with the side of the dish, thus short-circuiting the battery and generating considerable heat in the electrodes. This had the effect of liberating and dissolving the brown deposit. The current was allowed to act for half an hour longer, when the dish was removed from the circuit, washed, dried, and weighed.

The precipitate was perfectly adherent, and showed no tendency to oxidise when washed with alcohol and ether. The following is a tabular statement of the results obtained :—

| No. | Ammonium oxalate. Grms. | Saturated borax solution. C.c. | Current. Ampère. | Time. Hours. | Iron taken. Grm. | Iron found. Grm. |
|---|---|---|---|---|---|---|
| 1. | 5 | 5 | 0·02 | 16 | 0·0938 | 0·0933 |
| 2. | 5 | 10 | 0·02 | 17 | 0·0938 | 0·0935 |
| 3. | 6 | 10 | 0·06 | 4 | 0·0938 | 0·0938 |
| 4. | 5 | 5 | 0·072 | 2 | 0·0938 | 0·0939 |
| 5. | 6 | 5 | 0·125 | 2 | 0·0938 | 0·0938 |

It will be seen from the above that the presence of borax facilitates the precipitation of iron in ammonium oxalate solutions. The cause of the appearance of the slight brown deposit and the extent to which it might cause an error in results will be investigated later.

#### II.—*The Determination of Nickel.*

The determination of nickel presented no difficulties. The greater part of the experiments with iron were per-

formed in an analogous way with nickel; in no case was carbon deposited with the nickel. When iron and nickel are deposited together as an alloy in the presence of organic compounds the nickel does not prevent the contamination of the precipitate with carbon.

#### III.—*Determination of Zinc.*

Nearly all the published methods for the electrolytic determination of zinc give fairly satisfactory results. The tendency of the metal to be deposited in a spongy condition and the liability to oxidation are the principal difficulties usually encountered.

The tendency to oxidation may be prevented by the presence of formic acid in the solution, which by the liberation of hydrogen with the metal exercises a reducing action.

By the electrolysis of zinc formate in the presence of formic acid, Warwick (*Zeit. Anorg. Chem.*, i., 291) did not succeed in obtaining a complete deposit. The deposit is greatly influenced by the presence of sodium formate in the solution.

To a solution of zinc sulphate 3 c.c. of formic acid were added, and the solution partially neutralised with 1 grm. of sodium carbonate. The entire solution was diluted to 150 c.c. and placed in a current of 0·02 ampère for three hours.

Taken, 0·0611 grm. zinc. Found, 0·0603 grm. zinc.

In a similar manner the following determinations were made :—

| No. | Formic acid. C.c. | Sodium carbonate. Grm. | Current. Ampère. | Time. Hours. | Weight taken. | Weight found. |
|---|---|---|---|---|---|---|
| 1. | 4 | 1·5 | 0·125 | 3 | 0·0611 | 0·0612 |
| 2. | 5 | 1·0 | 1·000 | 3 | 0·0611 | 0·0611 |
| 3. | 5 | 1·0 | 0·050 | 3 | 0·0611 | 0·0611 |

The deposit adhered well, was compact and evenly distributed on the surface of the dish; the colour was light grey, in some cases almost metallic in lustre. As will be seen from the figures, a considerable variation in the strength of the current is allowable. This method is not allowable in the presence of the metals of the hydrogen sulphide group, as well as in the presence of iron, nickel, and cobalt.—*Journal of the American Chemical Society*, xviii., No. 7, July, 1896.

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## THE PRACTICAL USE IN THE CHEMICAL LABORATORY OF THE ELECTRIC ARC OBTAINED FROM THE LOW POTENTIAL ALTERNATING CURRENT.

### By MILO S. WALKER.

In this paper the author does not claim to have discovered any action of the electric arc that is not already known to chemists, but he will attempt to give a few suggestions as to the way in which the highest temperature at our command can be obtained and used in every chemical laboratory supplied with a fixture for incandescent lighting. Many colleges and secondary schools are equipped with these fixtures, and others can obtain them at but little cost. There is no practical reason why they should not be used for some experiments that cannot be performed with a Bunsen burner or a blowpipe.

The alternating current of about 50 volts and 1 to 5 ampères, now generally used for incandescent lighting, furnishes an excellent arc for chemical experimentation. It is very efficient, and can be handled easily and safely even by beginners in laboratory work.

The apparatus required consists of an iron or wooden stand, a screw clamp like those used for holding burettes, insulated copper wire, some electric light carbons, and a rheostat.

A piece of the so-called 10-ampère flexible lamp-cord

may be connected at one end with a plug set into the socket intended for an incandescent lamp. The two parts at the other end of the twisted cord are left free. Besides the lamp-cord, two pieces of ordinary insulated copper wire of medium size (about No. 20) and 70 c.m. long will be needed. These wires can be supplied and fixed as directed by any dealer in electrical supplies.

The rheostat is the most important part of the apparatus. Any commercial rheostat capable of carrying 12 ampères will answer all ordinary purposes. It may be necessary in large buildings, where one transformer supplies 100 lights or more, to use an additional resistance. About 40 feet No. 13 German silver wire has been found very satisfactory in a building where 175 lights are used.

The adjustable rheostat is essential to the proper control of the current, and to prevent too high heating of the wires and consequent melting of the safety fuses when the arc is started. All the experiments are started with a high resistance which is lessened until the proper arc light is obtained.

The assorted carbons are $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. The cored carbons are much better than the ordinary uncored ones. For obvious reasons "coppered" carbons should not be used. Carbons differ much in quality. Some contain considerable quantities of carbides and carbonates of metals. Those manufactured for use in optical projection usually contain less of these substances and give the best results.

The operator should not touch any metallic fixtures connected with the earth while he is working with the apparatus, as serious shocks may be received if the transformer is not properly insulated, a defect not uncommon in electrical work. It is better to work at a table on which there are no gas or water fixtures. Gas should be conducted to the table by a rubber tube connected with a gascock so far removed that there is no danger of touching any part of the apparatus and the gas-cock at the same time. There seems to be no other danger in working with the 50-volt alternating current. The students

c.m. Fix into a wooden clamp, and connect with insulated wire like the other carbon. On account of the heat an iron clamp with insulated handle is better for some experiments. Connect all wires so that the circuit will be completed if the carbons are allowed to touch each other. As the light is intense the eyes should be protected by a dark or blue glass. The longer carbon is stationary. The movements of the shorter carbon are controlled like a test-tube and holder. The rheostat should be adjusted so that an arc $\frac{1}{16}$ to $\frac{1}{8}$ inch long can pass between the lower end of the longer carbon and the ege of the conical cavity in the smaller carbon. A small piece of the substance to be tested can be placed in the cavity. Most minerals and common metals fuse easily. A piece of quartz $2 \times 1$ m.m. fuses completely. A piece the size of a pea fuses on one side.

As this contribution is intended only to show how the electric arc can be obtained and used in a chemical laboratory, a description of experiments is omitted, except where they show the method of working. The apparatus has not been in use long enough to show all its possible applications, or even a small part of them. But it has been shown that many of the remarkable experiments of Moissan can be repeated on a smaller scale by this simple apparatus. His work suggests much that can be done in the ordinary chemical laboratory lighted by "incandescent lamps."

If iron, copper, or manganese ores are placed in the conical cavity, the metals are formed containing small quantities of carbides.

For reduction of oxides it is better to substitute for the solid upper carbon, a carbon tube made by removing the core from the "cored carbon" 3 or 4 c.m. long. This tube is then fastened into a brass tube of about the same outside diameter, but with a large bore. The joint can be made gas-tight by a paste of pure graphite and water. The brass tube is fixed and connected with wire like the upper carbon in the other apparatus. The end of the carbon tube should occupy the position of the lower end of the larger carbon as indicated above. Now a gas can
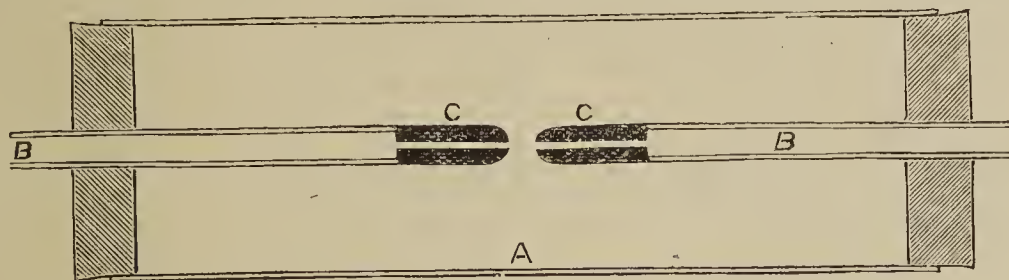


working in this laboratory somtimes receive shocks, but they generally consider shocks less disagreeable than accidental burns incident to work in general chemistry.

The electric arc can be used for the following purposes :—

1. To show the effect of high temperatures upon difficultly fusible and "non-volatile" substances.

2. For reduction of oxides of metal.

3. As a partial substitute for the blowpipe in qualitative analysis.

4. For the synthetic preparation of some compounds of carbon from the elements.

There is a wide range of experiments showing the effect of the electric arc upon substances almost infusible by other means.

The apparatus can be arranged in a variety of ways depending upon the experiment. For general use it may be arranged thus :—Fasten a cored carbon, about 10 × 1 c.m., in a vertical position so that the lower end is about 10 c.m. from the top of the table. Connect by wrapping with insulated copper wire, stripped where contact is made with the carbon. Bore a conical shaped cavity 4 or 5 m.m. deep in one end of another piece of cored carbon 4 × 1

be passed through the carbon tube so that it will strike a substance in the cavity of the small carbon while the arc is passing. Hydrogen or coal-gas may thus be conveniently used to prevent oxidation of metals while cooling, and seem to assist in reducing oxides and chlorides while the arc is passing. If carbon dioxide is used, carbon monoxide is formed with apparent increase in the reduction of oxides. In all these experiments a crater is gradually formed, and the arc generally passes from the inside of the carbon tube, thus giving maximum efficiency. When oxygen is used, the crater forms rapidly and enlarges to the full diameter of the carbon. Carbon monoxide is the main product of the quite rapid combustion, and acts as a powerful reducing agent upon an oxide in in the cavity of the other carbon. By reducing with carbon monoxide in this way, and cooling in hydrogen, quite pure manganese has been obtained from pure manganese dioxide. Similar experiments with oxides of other metals will be tried as soon as pure materials are secured.

Experiments with the electric arc are particularly interesting to the student, because he is able to get quick, sharp, and definite results. The manipulation is so easy

that young students can obtain beads of copper, iron, or manganese after a few minutes' practice. The electric arc has been used in this laboratory as an aid in qualitative analysis and a partial substitute for the blowpipe, but the method will not be described at present because it has not been sufficiently tested. A special apparatus has been used in which the electric arc is inside a partially closed glass tube, and the volatile constituents of the substance to be treated are collected and partially separated on the sides of the glass. The results so far obtained are very satisfactory.

Some experiments on the synthesis of the hydrocarbons from their elements have been tried. Thus acetylene is easily prepared by the method of Berthelot (*Comptes Rendus*, liv., 640) modified by Dewar (*Proc. Roy. Soc.*, xxix., 188).

The apparatus may be made as follows :—

Fit a gas tight cork into each end of a straight lamp chimney. Pass brass tubes 1 c.m. diameter and 15 c.m. long through each cork. Into one end of each tube fix a tube of carbon 3 c.m. long, prepared and fitted as shown under experiments for reduction of oxides. The joints of carbon and brass tubes should be gas tight.

Fit the corks and brass tubes so that the ends of the carbon tubes are nearly together, test the apparatus for gas leakage, turn on the current and again test after the heat has reached a maximum. If air-tight pass a stream of hydrogen through the brass and carbon tubes. After the oxygen in the apparatus has been consumed it may be necessary to increase the current.

As there is nitrogen in the air from the apparatus, small quantities of hydrocyanic acid are formed at first along with acetylene. The yield of acetylene is not large, but the method seems to be fully as satisfactory as the usual laboratory method of preparation of this gas from coal-gas by burning it in an insufficient supply of air. This is recommended as a laboratory method for students. It is the only experiment showing synthesis of carbon and hydrogen from the elements, and the construction and manipulation of apparatus are not too difficult for any one who has had a few weeks' experience in a laboratory.—*American Chemical Journal*, vol. xviii., No. 4.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.
*Ordinary Meeting, June 18th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. J. K. Burbridge and James Proude were formally admitted Fellows of the Society.

A certificate was read for the first time in favour of Mr. Hugh Manners, Academy House, Airdrie, N.B.

Dr. Tate was reinstated as a Fellow of the Society.

The following were duly elected Fellows of the Society :—Messrs. Robert Addie, John Caley, Charles Matthew Crossmann, B.Sc, Llewellyn John Davies, Leon Felix Goldstand, LL.D., Ralph Hamilton Hanger, Frederick William Harris, Ernest George Hill, B.A., Joshua Arthur Hughes, John Burnett Knight, Herbert E. Law, William Arthur Finch Lethbridge, B.A., Cecil Rudolf Lidgey, Percy Sykes Marshall, William McConnell, jun., Loxley Meggitt, Asutosh Rai Bahadur Mitra, James Stanley Muir, B.Sc., James Hadden Overton, Hastings Montague Page, Arthur Payne, Sigmund Georgjewitsch Rosenblum, Samuel Thomas Skelton, George Egerton Scott Smith, Douglas Stuart Spens Stuart, B.Sc., James Whitehead.

Of the following papers those marked * were read :—

*75. "*The Action of Bromine on Pinene with reference to the Question of its Constitution.*" By W. A. TILDEN, D.Sc., F.R.S.

Experiments made by the author in 1888 led him to believe that pinene combines not only with two atoms, but with four atoms of bromine. This conclusion was confirmed by the independent experiments of Stschukareff in 1893. Wallach, however, maintains that pinene can unite with only two atoms of bromine, and the various formulæ proposed by different chemists for this hydrocarbon are based on that assumption. The author has, therefore, undertaken a fresh inquiry, as the result of which he is confirmed in his original opinion that pinene combines directly with four atoms of bromine, the amount of bromine entering the molecule by substitution for hydrogen being comparatively insignificant. He therefore proposes for pinene a formula,—

$$CH_2 \cdot C \cdot CHCH_3$$
$$| \quad || \quad |$$
$$C_3H_7CH \cdot C \cdot CH_2 \quad ,$$
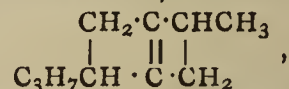
derived from a ring of six carbon atoms with a *double* para-linkage, the disruption of which at once gives a cycloid closely related to benzene, and accounts for the ready formation of cymene, &c.

*76. "*Preliminary Note on some Products from Pinene Tetrabromide.*" By W. A. TILDEN, D.Sc., F.R.S., and A. NICHOLLS.

The liquid tetrabromide formed by the addition of pinene to four atoms of bromine, as described in the preceding paper, is a very unstable compound, for it begins to evolve hydrogen bromide soon after its formation if kept at or near the temperature of the air. In order to investigate the products of this decomposition, a considerable quantity of the bromide was prepared. From the resulting colourless solution the carbon tetrachloride was distilled by a water-bath, and the residual liquid subjected to distillation alone with the object of expelling as much as possible of the hydrogen bromide, which escaped for the most part as gas. A colourless distillate was obtained, leaving a small quantity of a brown oily residue, which boils at a high temperature with further decomposition. On re-distilling the perfectly colourless distillate under pressure reduced to about 10 m.m., it came over between 125° and 175°, leaving a small additional quantity of the dark residue, from which, after standing a few hours or days, a crystalline substance was deposited, which was identified by analysis and melting-point as Wallach's dibromide, $C_{10}H_{16}Br_2$, m. p. 169—170° (*Annalen*, cclxiv., 7).

In order to decompose the last portions of bromide in the distilled liquid, it was heated with excess of aniline to the boiling-point of the latter, and subsequently steam distilled. The distillate, acidified with dilute sulphuric acid in order to fix the small quantity of aniline present, and again steamed, gave a colourless hydrocarbon lighter than water. By fractionation, this was found to yield a portion boiling at 155—157°, which contains solid camphene crystallisable by cooling. The larger part comes over between 158° and 162°, and deposits no solid at −15°. Smaller fractions up to 185° were obtained, and these remain to be examined. The chief fraction, 158—162°, reduced aqueous solution of permanganate at 16—18°, and fixed a quantity of bromine corresponding approximately to $Br_2$ for $C_{10}$.

As with the quantity of hydrocarbon at our command it seemed improbable that a fraction could be separated in a pure state, it was thought best to submit the liquid to oxidation. Two portions, the product of one preparation of bromide, were taken, namely, 30 grms., boiling between 155° and 160°, from which the camphene had been frozen out as completely as possible, and 30 grms. boiling between 160° and 170°. Oxidation with aqueous permanganate at a temperature which never rose above 26° gave the same chief product, and the two products were therefore supposed to contain a common ingredient. The unchanged hydrocarbon and precipitated oxide of manganese having been removed, the clear solution was mixed with a quantity of sulphuric acid calculated to

neutralise the alkali contained in it. A white cloud made its appearance, which was removed on shaking with ether. The ethereal extract, submitted to distillation, left a watery residue, in which floated a nearly colourless oil of about the same density as water. The 30 grms. of hydrocarbon at 155—160° gave 7·5 grms. of this fluid, and the 30 grms. at 160—170° gave 6 grms. This substance is a well-marked acid, having a sour and astringent taste; it decomposes carbonates, and when mixed with solutions of soda develops much heat. Distilled under a pressure of 20 m.m., it partly passed over at 200—210°, but evidently undergoes decomposition. It yields a crystalline slightly soluble sodium salt. A solution of this salt gives with copper sulphate a greenish precipitate, which seems to be a basic salt, and with silver nitrate a white precipitate, which becomes brownish on exposure to light, but does not blacken on boiling. Analyses were made of the acid (left in a vacuum till it ceased to lose weight) and of the crystallised sodium salt, with results corresponding to the formulæ $C_{10}H_{16}O_3$ and $C_{10}H_{15}NaO_3$.

This compound does not appear to be a ketonic acid, and the remarkable properties of its sodium salt lead to the suspicion, notwithstanding that it has not yet been crystallised, that it may be identical with Baeyer's nopic acid, a by-product recently obtained in the oxidation of crude pinene by permanganate (*Ber.*, xxix., 25). This, however, can only be settled by further inquiry, for which materials are already partly prepared.

*77. "An Apparatus for showing Experiments with Ozone."* By G. S. NEWTH.

The special feature of this apparatus consists in the device for introducing reagents into the ozonised oxygen without disturbing the volume of the gas. The reagent is contained in a sealed capillary tube, which is retained in position by means of four small raised points of glass upon the walls of the inner and outer tubes of the ozone apparatus. The inner tube is ground to fit the outer one, and by a slight turn of the former the tube containing the reagent can be broken. In this way it is possible to show that the contraction in volume due to the absorption of ozone by turpentine is exactly twice as great as that which is produced by ozonising the oxygen, and also that when ozone is acted upon by potassium iodide a volume of oxygen equal to that of the ozone is liberated.

*78. "Note on Santalal and some of its Derivatives."* By ALFRED C. CHAPMAN, F.I.C., and HERBERT E. BURGESS.

In connection with a study of certain hydrocarbons allied to the sesquiterpenes, upon which one of the authors is engaged, it became a matter of interest to determine more carefully the chemical properties of cedrene, and to compare it with the hydrocarbon obtained by the action of phosphorus pentoxide on santalal, with which it is generally said to be identical.

The cedrene was prepared by the fractional distillation of about 1 litre of cedar-wood oil under reduced pressure, and had a corrected boiling-point of 261—262°. Its density at 15°/15° was 0·9359, and it produced, in a 100 m.m. tube, a lævorotation of 60°. Its refractive index for the red hydrogen line and for the sodium line was $\mu H_a = 1·4991$; $\mu D = 1·5015$.

Although cedrene is unsaturated, and combines readily with hydrogen chloride and bromine, no definite compounds with these substances could be isolated. Negative results were also obtained in the case of the oxides of nitrogen and nitrosyl chloride.

Santalal was next prepared by the fractional distillation of santal-wood oil. Its corrected boiling-point was found to be 301—306°, some decomposition occurring at this temperature. Its density was $d\ 15°/15° = 0·9793$; $d\ 20°/20° = 0·9761$, and its specific rotatory power at 27° was $-14°\ 42'$ for sodium light.

Its refractive index for the lines C and D was $\mu H_a = 1·5051$; $\mu D = 1·5085$. Its specific refractive energy

is, therefore, 0·3039, and its molecular refractive energy 66·8. $C_{15}H_{24}O$ requires 66·3. Its general properties are those of an aldehyd.

On oxidation with an aqueous solution of potassium permanganate it yielded an acid crystallising from dilute alcohol in thin pearly plates melting at 76°. For this substance the name "santalenic acid" is suggested. This acid is still under investigation.

From santalal the hydrocarbon, $C_{15}H_{22}$, was prepared by treatment with phosphorus pentoxide and subsequent fractionation under reduced pressure. The main fraction was then obtained as a colourless liquid boiling between 140—145° (25 m.m.). Its density at 15°/15° was 0·9359. In a 100 m.m. tube at 16° it produced a rotation of 5° 45' to the right. This hydrocarbon is unsaturated, combining directly with hydrogen chloride and bromine, but no definite compound could be obtained. Attempts to prepare compounds with the oxides of nitrogen and nitrosyl chloride were equally unsuccessful.

So far as these results go they show that cedrene and the hydrocarbon from santalal are very similar, but not identical.

*79. "Second Note on the Liberation of Chlorine during the Heating of a Mixture of Potassic Chlorate and Manganic Peroxide."* By HERBERT MCLEOD, F.R.S.

This paper is a reply to a criticism by O. Brunck (*Zeit. Anorg. Chem.*, 1895, x., 222) on a previous note, in which it was shown that chlorine is produced by heating a mixture of potassic chlorate and manganic peroxide. Brunck considers that the evidence is insufficient, and that the author was misled by the presence of potassic chloride mechanically carried over by the gas. Further experiments have been carried out in a different manner, arising from a suggestion of Dr. Armstrong. The mixture of potassic chlorate and manganic peroxide was heated in a test-tube by the vapour of boiling mercury, and the gas passed into an exhausted flask. After the lapse of some days, during which the suspended matter settled, the gas was pumped out through U-tubes containing solutions of sodic carbonate and potassic iodide. When the gas traversed the sodic carbonate first, no colouration was seen in the potassic iodide, even when this was done immediately after the gas was collected, showing the absence of ozone. On acidifying the sodic carbonate solution with nitric acid, and adding argentic nitrate, a precipitate of chloride was formed which was weighed, and from it the quantity of chlorine was calculated. In three experiments the quantities of chlorine were 0·064, 0·063, and 0·057 per cent on the quantity of potassic chlorate used. When the gas, after three days' rest, was passed through a solution of potassic iodide and then through sodic carbonate, the latter did not contain chloride, and the former solution was coloured; on determining the liberated iodine volumetrically it was found to correspond to a quantity of chlorine equal to 0·063 per cent on the chlorate. Sodic hydrate solution that was used for washing oxygen, prepared by heating the usual mixture, was found to contain permanganate, some oxides of manganese having been mechanically carried into the solution, showing that the gas contained chlorine, for ozone does not produce permanganate when in contact with sodic hydrate containing manganic peroxide.

*80. "Polymorphism as an Explanation of the Thermochemical Peculiarities of Chloral and Bromal Hydrates."* By WILLIAM JACKSON POPE.

Berthelot has observed that the heat of combustion of chloral hydrate decreases as the time elapsing since fusion and solidification of the sample increases; the same observation has been made by Bruner respecting bromal hydrate. No explanation of this peculiarity is offered by either of these chemists, although Bruner states that other substances such as thymol and menthol, which are pasty after solidification, do not show the same behaviour.

In the case of chloral hydrate at least, the explanation

of the gradually decreasing heat of combustion is a purely crystallographic one. On cautiously melting the hydrate on a microscopic slide under a cover slip, and allowing the slide to cool, solidification readily occurs, and a thin crystalline film of the substance suitable for micro-crystallographic examination is obtained; it consists entirely of felted acicular crystals, most of which are so orientated that the optic axial direction of an optically negative uniaxial substance is perpendicular to the surface of the slide; in other crystals the optic axis emerges obliquely, and sometimes the crystals are slightly biaxial. A few of the needles may be truly biaxial, but this can hardly be stated definitely. After several hours at the ordinary temperature, minute rhomboidal plates make their appearance amongst the needles, and, after twenty-four hours, have become sufficiently large for crystallographic examination. The number and size of these plates, which belong apparently to the monosymmetric system, increase continuously, whilst the number of needles decreases until, after six or eight days, none but the monosymmetric plates remain. It is thus evident that on solidification of chloral hydrate a uniaxial form is obtained which very slowly changes into a biaxial modification stable at ordinary temperatures; this change must be accompanied by an evolution of heat, as are all changes of the kind, so that freshly solidified chloral hydrate has a larger heat of combustion than a sample solidified several days before burning. The change of any particular spot in the slide may be best observed and recorded photographically, and several good series of micro-photographs have been taken between crossed Nicols at definite intervals of time, which show the transition in a very perfect manner.

On similarly examining bromal hydrate, no very distinct evidence of change is obtained, the solidified mass being scarcely suitable for micro-crystallographic examination. The photographic record, however, seems to indicate a change of some kind in the plate.

The thermo-chemical behaviour of thymol must, as found by Bruner, be quite normal, because no crystalline change of any kind occurs in it after solidification has once occurred.

After melting menthol, the other instance quoted by Bruner, it solidifies from centres giving a radially crystallised film. There is usually just time to give a photographic plate an exposure of three minutes on the preparation, however, before a change of crystalline form sets in and the menthol becomes rapidly converted into a mass of very minute crystals which show aggregate polarisation; after this no further change occurs. Since the time elapsing between cooling and the formation of the crystalline modification of menthol stable at ordinary temperatures is too short to allow of the substance being weighed and introduced into the calorimetric bomb, the heat of combustion determined has always been that of the modification stable at ordinary temperatures.

The crystallographic examination of these substances shows that thermo-chemical data respecting solid organic substances should always be accompanied by a crystallographic description of the material used.

81. "*Explosion and Detection of Acetylene in Air.*" By FRANK CLOWES, D.Sc.

The behaviour of mixtures of air with gradually increased proportions of acetylene, when brought into contact with flame, were studied by a method recently described by the author.

The method enables mixtures in varied and accurately known proportion to be rapidly prepared. The proportion of acetylene was progressively increased from 1 to 82 per cent.

The mixture containing 3 per cent of acetylene was the first which was affected by contact with the flame placed either above or below. A pale green flame slowly traversed the mixture, showing that it was feebly explosive. As the proportion of acetylene was increased, the rapidity of combustion increased, and even a small volume of the mixture gave decidedly explosive effect.

When 22 per cent of acetylene was present, the explosive combustion of the mixture was attended with a slight separation of unburnt carbon. As the proportion of acetylene was increased, the separation of carbon was more marked. The limit of explosibility, as judged by the flame traversing the mixture, was reached when 81 per cent of acetylene was present.

The range of explosibility of mixtures of air with acetylene, extending from 3 per cent of acetylene to 81 per cent, is extraordinarily wide, exceeding that of any combustible gas yet experimented with. It seems highly probable that the appearance of combustion extending through the mixture with the higher proportions of acetylene is partly due to acetylene being an endothermic compound. Accordingly, the combustion of a small portion of the acetylene in contact with the kindling flame, starts the decomposition of the remainder of the acetylene, with the production of heat and the appearance of combustion. This probably explains why air containing much acetylene becomes heated throughout, when it is kindled at one point, and thus extends the range of explosibility of mixtures of acetylene with air.

In estimating the percentage of acetylene in air, if the amount does not reach the lower explosive limit of 3 per cent, the most convenient method was the passage of the air over a standard hydrogen flame, and an examination and measurement of the halo or "flame-cap" which was seen in a darkened room over the hydrogen flame. A laboratory apparatus suitable for this purpose is nearly perfected, and will probably be found convenient as a means for measuring accurately the percentage of any combustible gas present in air. About 600 c.c. of the mixture are required for the estimation, which is completed in a few seconds.

When air containing less than 3 per cent of acetylene was passed over the standard 10 m.m. hydrogen flame, the flame at once became yellowish green in tint. A halo or "cap" was at the same time seen, the height of which increased so rapidly with the increase in the percentage of acetylene, that the last estimation was made by the use of a reduced 5 m.m. hydrogen flame. The measurements of the "cap" over the 10 m.m. hydrogen flame were as follows:—0·25 per cent, 17 m.m. cap; 0·5 per cent, 19 m.m.; 1 per cent, 28 m.m.; 2 per cent, 48 m.m. Over the 5 m.m. flame, 2·5 per cent gave 56 m.m. cap, and 2·75 per cent 79 m.m. cap. When the percentage reached 3 per cent it burnt throughout, giving no cap.

82. "*On the Occurrence of Quercetin in the Outer Skins of the Bulb of the Onion (Allium Cepa).*" By A. G. PERKIN and J. J. HUMMEL.

Zeuch (*Farben und Farbenkünde*, 1825, i., 434) has described the dyeing properties of these skins. The colouring matter was obtained by the authors in the form of glistening yellow needles of the formula $C_{15}H_{10}O_7$, which yielded compounds with mineral acids, the sulphuric acid compound $C_{15}H_{10}O_7,H_2SO_4$ was analysed. On acetylation, a compound, $C_{15}H_5O_7(C_2H_3O)_5$, forming colourless needles, melting-point 190—191°, was obtained, and by decomposition with fused alkali, phloroglucin and protocatechuic acid formed the principal products. With mordants it dyed shades similar to those given by quercetin, the colouring matter of quercitron bark, and was thus proved to be identical with this substance.

Comparative dyeing experiments showed that the colouring matter of onion skins was quite equal to that of such well-known dye-stuffs as old fustic and quercitron bark.

(To be continued).

Exhibitionism.—We regret to learn that Queensland is preparing to hold an "International" Exhibition. Had it been purely Imperial it would have had our best wishes.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 5, August 3, 1896.

**Study of the Diamantiferous Sands of Brazil.**—Henri Moissan.—Thanks to the kindness of Professor Lacroix, of the Museum of Natural History, we have been able to examine if the diamantiferous sands of Brazil contain also microscopic diamonds. 4500 grms. of the sand were sifted and yielded 1350 grms. of a powder consisting almost entirely of silica. The attack is very tedious, and it is only after a dozen alternate treatments with hydrofluoric acid and boiling sulphuric acid that we arrived at a residue of 2 grms. The substance is then treated with melting fluopotassium hydrofluoride, and is then attacked with potassium bisulphate, when we obtained a residue of 2 grms. This residue contains portions consisting of small transparent grains, some spangles of native gold and platinum, and of small black brilliant crystals having the aspect of graphite. We separated some of the latter and transformed them into graphitic oxide, which on deflagration yielded pyrographitic oxide. After having characterised the graphite all the residue was treated with methylene iodide. The portion more dense than this liquid was treated anew with fluoride hydrofluorate and then with bisulphate. An attack with aqua regia caused the precious metals to disappear. We have then been able to separate some black fragments and transparent fragments which had no action upon polarised light and which burnt completely in oxygen, yielding a white precipitate with baryta water. This residue contains brilliant grains acting upon polarised light, having an elongated form, a corroded surface, and which have been ultimately caused to disappear by successive attacks. This Brazilian diamond contains black diamonds of a shagreened surface, also transparent diamonds of irregular form, and lastly graphite. There exist, therefore, in nature, both at the Cape and in Brazil, microscopic diamonds, black or transparent, and in both cases accompanied with graphite.

**Oxidation of the Organic Matter of the Soil.**—P. P. Dehérain and E. Demoussy.—Although it is at temperatures exceeding 100° the oxygen of the air burns rapidly the organic matter of the soil, oxidation is fairly active between 40° and 60°; we can thus understand how in hot regions lands ploughed but left without manure become barren by the disappearance of the humus which the spontaneous vegetation had accumulated. In our cool regions this disappearance is slower; still the fields of the experimental farm of Grignon, bearing various crops and left without manure, lose in ten years the half of their organic matter. If the soil is plentifully manured the oxidation is, in our opinion, too slow, whence the incessant work which farmers have to undertake to allow the oxygen to penetrate into the soil and to bring the humus into such a state that nitrification can be effected.

**Biological Chemistry and Mechanics.**—A. Chauveau deals with the following subjects :—What we must think of the alleged sterile dissipation of energy in the execution of muscular work. Extension of the Applications of the law of energetic equivalence in biology. Not adapted for insertion.

**Non-Refraction of the X Rays by Potassium.**—F. Beaulard.—One of the most important characters of the X rays is that they are not refracted, or at least that they do not undergo any refraction perceptible and capable of easy measurement with our present appliances. The very precise researches of M. Gouy (*Comptes Rendus*, May 26th and July 6th) have shown that aluminium does not refract the X rays and that the refraction, if it exists, is insensible.

$$\left( n - 1 < \frac{1}{10^6} \right)$$

The author has attempted to refract the X rays through a prism of potassium. The result was negative; the deviation, if existing, is less than 10″; the index therefore differs from unity by a quantity inferior to 1/10,000th.

**Nitrogen and Argon in Fire-damp and in the Gas of Rochebelle.**—Th. Schlœsing, jun.—(See p. 87).

**Specific Heat of Sulphur in the State of Viscosity.**—J. Dussy.—The specific value of viscous sulphur is distinctly higher than it presents in the liquid state. The curve which represents $2\frac{T}{o}$ (the total heat lost by 1 grm. of sulphur in passing from T to 0°) seems to experience a change of pace about 230°. The author hopes to extend the same study to selenium. Sulphur, if tempered at heats comprised in an interval between 157° and 175°, solidifies very rapidly, taking a characteristic vitreous aspect, which does not seem to have been as yet pointed out. Thus sulphur cast at 165° solidifies in filaments, with a distinctly vitreous fracture; a mass of sulphur at 220°, thrown at once into cold water and then left to itself, presents after solidification an external layer of soft sulphur, then a vitreous layer, and finally a layer of prismatic sulphur. We generally approximate soft sulphur to vitreous selenium. The existence of vitreous sulphur legitimates this approximation more completely.

**Contributions to the Study of the Analytical Characters of the Compounds of Tungsten.**—E. Defacqz. (See p. 88).

**Action of Aluminium Chloride upon Benzene containing Thiophene.**—Eyvind Baedtker.—If we heat crystallisable benzene with aluminium chloride on the water-bath we observe at a low temperature the formation of hydrogen sulphide and hydrochloric acid, and if we collect the vapours given off in a solution of lead acetate, lead sulphide is precipitated.

**On New Mixed Trimethylenic Compounds.**—Louis Henry.—The compounds obtained are trimethylene chloro-iodide, $ClCH_2 - CH_2 - CH_2I$, and trimethylene nitro-chloride, $ClCH_2 - CH_2 - CH_2(NO_2)$.

**Rapid Determination of the Components of a Mixture of Primary, Secondary, and Tertiary Amines having the same Aliphatic Radicle.**—Ch. Gassmann.

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# MISCELLANEOUS.

**Various Methods of Formation of Blue Nitro-disulphonic Acid and of its Salts.**—Paul Sabatier.—As the author has previously shown, we can obtain the blue acid by causing a regulated mixture of nitric oxide and of air to react upon sulphuric acid saturated with sulphurous anhydride. But it may also be obtained by the reduction of the nitrosulphuric liquid, by the action of sulphurous acid upon nitrosulphuric liquid, and by the action of nitric oxide upon a metallic sulphate in a sulphuric solution.—*Comptes Rendus*, cxxiii., No. 4.

**Behaviour of Gold in Pyrites during Weathering.**—W. Mietzchke.—Auriferous pyrites, whether in solid rock or in a loose condition, display the peculiar behaviour that the gold uniformly distributed in the mass in the state of sulphide, in proportion as it is converted into an oxidised product, moves towards the middle of the mass. Hence the pyritic nucleus of a half-weathered crystal shows double the proportion of gold than does the average mineral before decomposition. In a fully weathered specimen the author found a granule of gold with crystalline surfaces. The confirmatory specimens were obtained from the Orenburg Government (Russia).—*Berg. u. Hütten. Ztg.* and *Chem. Zeitung.*

**A Filter of Cellulose.**—Henri Pottevin.—With fibres of cellulose, finely pulverised and sifted, and suspended in water, we obtain a paste which, if allowed to dry slowly, gives plates which in the thickness of a few m.m. are capable of serving as a substitute for porcelain. These plates, for filtration, must be kept between two layers of stoneware or of perforated metal. Filtration through such plates, arranged like a filter-press, was found to sterilise water.—*Comptes Rendus,* cxxiii. No. 4.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1918.

## ACTION OF HYDROGEN SULPHIDE ON CUPRIC SALT SOLUTIONS.

By BOHUSLAV BRAUNER, Ph.D., F.C.S.,
late Berkeley Fellow of Owens College.

MR. COPPOCK'S paper in one of your recent issues (CHEM. NEWS, vol. lxxiii., p. 262) induces me to give a short account of my experience on the above subject.

The fact that the black precipitate obtained from cupric solutions by the action of hydrogen sulphide is $Cu_4S_3$, and not $CuS$, is not due to Menschutkin, but—as the author seems to be unaware—to Julius Thomsen, who, in 1878, published a short paper on that subject (*Berichte*, xi., p. 2043).

Several years ago I undertook, with Mr. A. Polan, a work on the above subject which gave only experimentally, but not theoretically, definite results, and which were never published; Mr. Polan having left the University meanwhile. The facts arrived at are the following:—

It was proved, first, that the said " black," but better, greenish black or dark olive-green, precipitate which is formed by the action of hydrogen sulphide in excess on a solution of a cupric salt and removing the excess of the gas by a current of carbon dioxide, really contains copper and sulphur in the exact atomic proportion $Cu : S = 1 : 1$; all the sulphur being, however, not combined to copper, but existing partly in the free state. But whereas in Thomsen's experiments cupric sulphate was precipitated with an excess of sodium sulphide—which dissolved the excess of free sulphur, forming a polysulphide—a different method was employed in our experiments.

Solutions of cupric sulphate or chloride in water:—(1) More or less dilute; (2) more or less acidified; and (3) either cold or at a higher temperature, were precipitated with (4) a slow or a rapid current of hydrogen sulphide in excess, i.e., completely.

In order to avoid a possible oxidation of the precipitate in the air, it was filtered, washed first with aqueous hydrogen sulphide, then in an atmosphere of carbon dioxide with water free from air, then with alcohol, repeatedly with distilled carbon disulphide, until all free sulphur was removed; again with alcohol, in order to remove any trace of carbon disulphide; and finally with ether, keeping the precipitate all the time in an atmosphere of carbon dioxide.

The completely washed and dried finely-divided precipitate undergoes an oxidation in the air, but this circumstance was quite immaterial in regard to the course of analysis used for ascertaining the composition of the dark olive-green powder obtained.

An unweighed quantity of the sulphide was brought into a wide-necked bottle; it was then moistened with water, some potassium chlorate was added, and a short test-tube containing fuming nitric acid was inserted, after which the bottle was closed with a moistened and well ground glass stopper, which was fastened with a cloth and string. By inclining the bottle, small quantities of nitric acid are poured out successively from the short test-tube (which possesses a small hole near its upper end, so that it is easily put in and out with a hooked platinum wire) upon the wet mixture of the copper sulphide with potassium chlorate (on using dry mixtures of some sulphides explosions take place). When every reaction in the cold has ceased, the bottle is opened and the oxidation completed at a moderate heat.

After removing all nitric acid by evaporation, finally with hydrochloric acid, the clear solution was brought to a definite volume, and two or more aliquot equal portions were measured out.

One part was used for the determination of copper, the other for the determination of sulphur, and from the relations of copper to sulphur the composition of the precipitate remaining after the above treatment was calculated under the plausible assumption that the precipitate contains only copper and *combined* sulphur, any *free* sulphur having been removed by the above process.

The results obtained may be shortly summed up as follows:—

1. The original precipitate, unwashed with $CS_2$, &c., always consists of copper, combined sulphur, and free sulphur.

2. The precipitate washed with $CS_2$, &c., never contains copper and sulphur in the atomic proportion $CuS$.

3. This precipitate contains copper and sulphur in very *varying* proportions expressed by the general formula $Cu_nS(n-x)$, in which always $x < \frac{1}{2}n$, i.e., its composition lies between that of $CuS$ and $Cu_2S$; it, therefore, does *not always* consist of Thomsen's $Cu_4S_3$.

4. It is interesting to find that the composition of the precipitate may be represented dualistically, as if it consisted of a mixture or compound of cupric sulphide with cuprous sulphide in definite proportions; the relative number of molecules being expressed by small integers. Further research must show whether this is not due to chance only. Such cases are, e.g., $5CuS + 2Cu_2S$, $3CuS + Cu_2S$, $2CuS + Cu_2S$, &c.

From the detailed study of the action of hydrogen sulphide upon solutions of arsenic and antimonic acids, as undertaken by Brauner and Tomicèk, Le Roy McCay, Brauner and Bosèk, it results that, as long as hydrogen sulphide is not present in excess, oxysulpho-compounds (sulphoxy-acids) of arsenic and antimony are formed, which, by the further action of hydrogen sulphide, owing to the formation of oxygen and sulphur compounds of the higher form $RX_5$ and the lower form $RX_3$, yield a mixture of the pentasulphide with the trisulphide.

In regard to the fact that—(1) In copper (and also nickel) is left a part of the property of forming soluble double sulphides (sulpho-salts), in which respect it approaches the more negative elements of the analytical arsenic-antimony group (Ge, Sn, As, Sb, Mo, Te, W, Pt, and Ir); and (2) that hydrogen or other sulphides when acting upon an excess of a cupric solution give rise to the formation of black or brown solutions, containing copper probably in a similar state in which antimony is contained in a mixture of an excess of antimonic acid solution with hydrogen sulphide; it may be concluded, by analogy, that in the first phases of the reaction compounds of the general formula $Cu_{(a+b)}S_aX_{2b}$ (where $X = Cl$, $\frac{1}{2}SO_4$, &c.) are formed, which further decompose as follows:—

$$Cu_{(a+b)}S_aX_{2b} = bCuX_2 + bCu_2S + (a-2)CuS + bS;$$
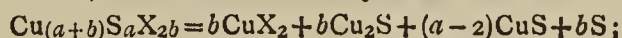
so that by a further action of hydrogen sulphide a mixture of cupric sulphide with cuprous sulphide results.

The experiments hitherto made have not yet yielded a sufficient material from which might be concluded whether the reaction is going in one direction (production of more $CuS$) or the other ($Cu_2S$), as the temperature is lower or higher, the current of hydrogen sulphide more or less rapid, and the quantity of acid present larger or smaller. This may be shown by further experiments, without, as I hope, trespassing on Mr. Coppock's ground of research.

Chemical Laboratory,
Bohemian University, Prague.

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**Examination for free Hydrochloric Acid in the Gastric Liquid.**—J. Sjögnist (*Scandin. Archiv. Physiol.*).—The author recommends a procedure which consists essentially in precipitating the dissolved baryta as chromate, and determining the chromic acid liberated by an acid by Zulkowsky's iodometric process.

## STUDY ON THE NITROGEN AND THE ARGON OF FIRE-DAMP.

### By TH. SCHLŒSING, Jun.

I HAVE the honour of presenting to the Academy a continuation of my researches on the composition of fire-damp. I have been led to study this gas as a product of the slow decomposition of vegetable matter in the particular case of its transformation into coal. I have at first attended to its combustible part; but soon the incombustible portion, or, more strictly speaking, the nitrogen and the argon of this portion, have seemed to me also of interest.

There is always nitrogen in fire-damp. Its proportion varies within very wide limits. In twenty-three specimens from different localities I have obtained as extreme ranges 0·75 and 30 per cent. Whence comes this nitrogen? It is, I think, most commonly admitted that it has been disengaged by nitrogenous constituents of vegetable matters which have passed into the state of coal. It seems very difficult to admit such an origin, for in slow decompositions reproduced in the laboratory we neither observe such a variability, nor, above all, such an exaggeration in the proportion of the nitrogen set at liberty. It was therefore natural to suspect the air as the possible source of the nitrogen of fire-damp. I examined if argon was present in this nitrogen, and I found 1·1 per cent—a proportion very near that (1·19) which characterises the nitrogen of the atmosphere. This seemed evidence in favour of the atmospheric origin of the nitrogen of fire-damp.

M. Leproux was aware of these results. To permit me to verify them, he offered me fire-damp from St. Etienne and Plat-de-Gier, which he knew was disengaged under a great pressure, and which, consequently, was derived from portions of the rock into which the air could not have penetrated in recent times. If the nitrogen of such fire-damp possessed the proportion of argon peculiar to atmospheric nitrogen, we might admit that the air to which it belonged had been imprisoned in the coal at the remote epoch when the fire-damp was formed; that is to say, according to the expression of M. Leproux we were in presence of *fossil air.*

Thus it became more and more interesting to determine exactly the proportion of argon contained in the nitrogen of fire-damp.

A first determination made on the fire-damp of Saint Etienne gave 1·18 argon per cent of nitrogen. This was exactly the same proportion as in atmospheric nitrogen. With a recommendation from M. Aquillon, the Inspector-General of Mines, I obtained fire-damp from various mining companies, taken as far as possible from blow-holes which yielded the gas at a considerable pressure.

Each specimen was collected by passing into series of four or six bottles, each of 6½ litres, a current of fire-damp which drove out the air by displacement. The bottles were then closed by means of good pinchcocks acting on good caoutchouc tubes. Collecting fire-damp over water must be avoided if we wish to reach great accuracy; for the water, which dissolves nitrogen and argon decidedly, but unequally, might alter the proportion of the two gases sought for, diminishing or increasing it, according to the cases.

To arrive at the proportion in question, it is necessary at first to separate the nitrogen along with its argon. To this end the fire-damp is passed over copper oxide heated to redness and then into potassa. For this operation I find it very advantageous to use an apparatus analogous to that which I have used for the determination of argon, in which a mercurial pump causes the gases to circulate constantly over the reagents. We introduce the fire-damp into the apparatus gradually, as it disappears until we have obtained a sufficient volume of nitrogen. A vacuum is made at the outset to eliminate the air, and again at the end to extract the nitrogen and bring it into a tube, where it is measured. Of this nitrogen we take a small specimen and determine its degree of purity eudiometrically. We generally find that it contains from 0 to 0·5 per cent of carbonic acid and of combustible gas, of which we take account in the calculations. We finally determine the argon thus prepared according to a process which I have already described. I have spoken of argon to simplify the description; but the true nature of the element determined is not absolutely established by the operations described. A spectral determination is required. I have made such a determination, making use of Plücker tubes, into which I introduced the gaseous residues in question with all the precautions requisite.

I cannot bring forward to-day all my results and my conclusions. I can merely say that in the nitrogen extracted from fire-damp I have always found a notable proportion of argon. But there follows a question to which an answer is required—Does the argon of fire-damp come from coal?

I have sought for argon in the coals of St. Etienne and of Plat-de-Gier.

The specimens analysed have been finely pulverised, then submitted to a vacuum and to a true determination of nitrogen of volume. The gas obtained was measured, verified as to its purity by eudiometric analysis, treated so as to isolate the argon: 22 grms. of coal (not dried) from St. Etienne yielded 243 c.c. or 3·304 grms. of nitrogen (say, by weight 1·38 per cent), which, after the operations required for separating the argon, left a gaseous residue of about 0·08 c.c. In like manner, with 18·3 grms. of the coal of Plat-de-Gier, I have obtained 196 c.c. or 0·245 grm. nitrogen (say, 1·34 per cent), whence there was extracted a residue of about 0·05 c.c. These residues are about equivalent to the argon which the atmospheric nitrogen might have furnished. They might further represent the foreign impurities in the substances analysed derived especially from the solutions of potassa, which had to be used in very important quantities.

In fine, the coals examined contained at most, if any, 1/200,000th of an element comparable to argon. It cannot, therefore, be thought that problematical traces of this element can exert an influence on the composition of the fire-damp.—*Comptes Rendus.* cxxiii., p. 233.

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## ASSAY OF GOLD ORES AND SANDS BY AMALGAMATION AND WITH THE BLOWPIPE.

### By HAMILTON MERRIT.

The author takes 1 kilo. of the material, passes it through a sieve of 60 meshes per square inch, and adds 1 oz. (31 grms.) of mercury and sodium amalgam. The latter prevents the excessive scattering of the mercury in the pan during amalgamation. The admixture of the mercury and ore is effected with a wooden pestle and is continued for an hour. The results obtained correspond approximately with those of amalgamation in the mill. Every grain of gold weighed represents 2 ozs. per ton. For decomposing the amalgam he uses, instead of a retort, sheet-iron moulded into the shape of a cup. The concentrates obtained are tested with the blowpipe quantitatively to ascertain if gold is still present. For a quantitative determination the grains are measured with Plattner's scale. In this manner ores may be used which contain not more than 60 marks of fine gold per ton.—*Inst. Amer. Mining Engineers*, Pittsburg Meeting, Feb., 1896, and *Chemiker Zeitung.*

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The Thalleioquin Reaction. — A. Belahoubek and Sedlecky (*Pharm. Post*).—The authors show that this reaction is interfered with by the presence of caffein or antipyrin.

## AN
# EMPIRICAL RELATION BETWEEN MELTING-POINT AND CRITICAL TEMPERATURE.

### By F. W. CLARKE.

ALTHOUGH many papers have been written upon relations between boiling-point and critical temperature, the melting-points of substances, at least in this connection, seem to have been little considered. And yet a glance at the subject will indicate its importance. For any substance the limits of the solid state are the absolute zero and the melting-point; while the extreme limits of the liquid condition are the melting-point and the critical temperature. A comparison of these values, therefore, will give for each substance the relative thermometric lengths of the two states of matter, and the results obtained, although empirical, have very decided interest. Unfortunately many of the compounds of which the critical temperature is known, have never had their melting-points determined, and hence the available data are very meagre.

Representing the ordinary melting-points by $t$ and the critical temperatures by $T$, the relation between them, on the absolute scale, is best represented by the formula—

$$\frac{T + 273}{t + 273}.$$

For the following substances this ratio is very nearly $= 2$; the data, except when otherwise stated, being taken from Landolt and Börnstein's tables. Fractions of degrees less than 0.5 are neglected.

|  | $t$. Degrees. | $T$. Degrees. | Ratio. |
|---|---|---|---|
| Nitrogen | −214.0 | −146.0 | 2.18 |
| Carbonic oxide | −207.0 | −139.5 | 2.02 |
| Argon (Olszewski) | −190.0 | −121.0 | 1.83 |
| Methane      ,, | −186.0 | − 82.0 | 2.19 |
| Hydrochloric acid | −112.5 | + 52.0 | 2.02 |
| Hydrogen sulphide | − 86.0 | +100.0 | 2.00 |
| Ammonia | − 75.0 | +130.0 | 2.03 |
| Benzene | + 3.0 | +288.5 | 2.04 |
| Acetic acid | + 17.5 | +322.0 | 2.05 |

In other words, for these nine substances the absolute melting-point is very nearly, if not exactly, one-half the absolute critical temperature, and the thermometric lengths of the solid and liquid states are approximately equal. Assuming the errors of observation to be evenly distributed in each case between the two temperature factors, we may average the latter and so compare the mean values with those actually recorded. The results are as follows:—

|  | Found. | | Average. | |
|---|---|---|---|---|
|  | $t$. Degrees. | $T$. Degrees. | $t$. Degrees. | $T$. Degrees. |
| $N_2$ | −214.0 | −146.0 | −211.0 | −149.0 |
| CO | −207.0 | −139.5 | −206.5 | −140.0 |
| A | −190.0 | −221.0 | −195.0 | −117.0 |
| $CH_4$ | −186.0 | − 82.0 | −180.0 | − 87.0 |
| HCl | −112.5 | + 52.0 | −111.0 | + 51.0 |
| $H_2S$ | − 86.0 | +100.0 | − 85.5 | +100.5 |
| $NH_3$ | − 75.0 | +130.0 | − 73.0 | +128.0 |
| $C_6H_6$ | + 3.0 | +288.5 | + 4.0 | +287.0 |
| $C_2H_4O_2$ | + 17.5 | +322.0 | + 22.0 | +317.9 |

When we consider the uncertainty of some of the measurements, the agreement is certainly very close.

This simple relation, however, is not general. In all, I have examined the data for about thirty substances, and no universal rule appears. There are, nevertheless, other regularities apparent which connect certain allied substances with one another, and two such groups I subjoin:—

|  | $t$. Degrees. | $T$. Degrees. | Ratio. |
|---|---|---|---|
| $C_2N_2$ | − 34.5 | +124.0 | 1.67 |
| $N_2O_4$ | − 10.0 | +171.0 | 1.64 |
| NO | −167.0 | − 93.5 | 1.70 |
| $N_2O$ | − 99.0 | + 35.5 | 1.77 |

These compounds run closely together, and are alike in being gaseous compounds of nitrogen. The next group contains five aromatic bodies.

|  | $t$. Degrees. | $T$. Degrees. | Ratio. |
|---|---|---|---|
| o-Xylene | −45.0* | +358.0† | 2.77 |
| m-Xylene | −53.0 | +346.0† | 2.81 |
| $C_6H_5Cl$ | −40.0 | +361.0 | 2.78 |
| $C_6H_5Br$ | −30.5* | +397.0‡ | 2.75 |
| $C_6H_5I$ | −28.5* | +448.0‡ | 2.94 |

\* v. Schneider.  † Altschul.  ‡ Young; theoretically determined.

Here, again, there is an essential identity of ratio with related constitution—a fact which suggests that the method of discussion applied to larger masses of data is likely to give information of considerable theoretical value.

For most of the other substances which I have considered, the ratio ranges between 2.2 and 3.0. For carbon dioxide its value is only 1.41; for ether it is 3.06. In the latter case the thermometric lengths of the solid and liquid states, therefore, are as one to two. A few bodies only give ratios higher than three. These are—besides ether—

| | |
|---|---|
| $CS_2$ | 3.36 |
| $PCl_3$ | 3.47 |
| Alcohol | 3.59 |

Other values are—

| | | | |
|---|---|---|---|
| $Br_2$ | 2.17 | $H_2O$ | 2.34 |
| $Cl_2$ | 2.44 | $SNCl_4$ | 2.47 |
| $SO_2$ | 2.22 | $CHCl_3$ | 2.62 |
| $CCl_4$ | 2.25 | $C_2H_4$ | 2.75 |

Paraxylene gives the ratio 2.14, varying widely from its isomers.

Concerning the quantity of heat necessary to raise a body from absolute zero to the melting-point, and then from the melting-point to the critical temperature, the data are altogether wanting; but the ratio between those two quantities would certainly be significant. For the regularities which I have here pointed out I have no theoretical explanation to offer. If, however, they serve to stimulate the determination of other low temperature melting-points for compounds of which the critical temperatures are known, this paper will have served a useful purpose. The relations which are already apparent cannot be meaningless, and others must be discoverable.—*American Chemical Journal*, xviii., No. 7, July, 1896.

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# THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

δ. *Not taking into consideration Volume Correction.*—The errors due to this in the measurement of gases are so great that in the case of gases the correction ought never to be overlooked. But even in the case of standard solution, overlooking this question of the volume correction may lead to unpleasant errors, as, for instance, is shown by the accompanying table drawn up by A. Schulze (Fresenius, *Zeit. f. Anal. Chemie*, 1882, p. 167):—

\* Read before the Iron and Steel Institute.

*Normal.*

| Temp. Degs. C. | Oxalic Acid. | Hydrochloric Acid. | Nitric Acid. | Sulphuric Acid. | Sodium Carbonate. | Caustic Soda. | Water in Glass. | Temp. Degs. C. |
|---|---|---|---|---|---|---|---|---|
| 5 | +0·0018 | +0·0017 | +0·0026 | +0·0025 | +0·0026 | +0·0028 | +0·0009 | 5 |
| 6 | 17 | 16 | 25 | 24 | 25 | 26 | 9 | 6 |
| 7 | 16 | 15 | 23 | 22 | 23 | 24 | 9 | 7 |
| 8 | 15 | 14 | 21 | 21 | 21 | 22 | 9 | 8 |
| 9 | 14 | 13 | 19 | 19 | 19 | 20 | 8 | 9 |
| 10 | 13 | 12 | 17 | 17 | 17 | 18 | 8 | 10 |
| 11 | 12 | 11 | 15 | 15 | 15 | 16 | 7 | 11 |
| 12 | 10 | 9 | 13 | 13 | 13 | 14 | 7 | 12 |
| 13 | 8 | 8 | 11 | 11 | 11 | 11 | 6 | 13 |
| 14 | 7 | 6 | 9 | 9 | 9 | 9 | 5 | 14 |
| 15 | 5 | 5 | 6 | 6 | 6 | 6 | 3 | 15 |
| 16 | 3 | 3 | 4 | 4 | 4 | 4 | 2 | 16 |
| 17 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 17 |
| 17·5 | 0·0000 | 0·0000 | 0·0000 | 0·0000 | 0·0000 | 0·0000 | 0·0000 | 17·5 |
| 18 | −0·0001 | −0·0001 | −0·0001 | −0·0001 | −0·0001 | −0·0001 | −0·0001 | 18 |
| 19 | 3 | 3 | 4 | 4 | 4 | 4 | 2 | 19 |
| 20 | 6 | 5 | 7 | 7 | 7 | 7 | 4 | 20 |
| 21 | 8 | 7 | 10 | 10 | 9 | 10 | 6 | 21 |
| 22 | 10 | 9 | 12 | 12 | 12 | 13 | 8 | 22 |
| 23 | 13 | 12 | 15 | 15 | 15 | 16 | 10 | 23 |
| 24 | 16 | 14 | 18 | 18 | 18 | 19 | 12 | 24 |

This table, which relates to the normal solutions mentioned at the temperature of 17·5° C., gives the correction for one cubic centimetre of the solution. The correction is therefore made by adding the product of the number of cubic centimetres used with the factor given in the table—observing whether it is a − or + quantity—to the number of cubic centimetres of the standard solution added in the course of the determination. Supposing, for instance, a titration had been made at a temperature of 12° C., and that 21 c.c. of normal sulphuric acid had been used, then $21 + 21 \times 0·0013 = 21·0273$ c.c. is the correct quantity of 17·5° C. If, on the other hand, 21 c.c. at the temperature of 24° C. was necessary, then $21 − 21 \times 0·0018 = 21 − 0·0378 = 20·9422$ c.c. of acid at a temperature of 17·5° C. If, again, a titration with normal sulphuric acid were effected once at a temperature of 12° C. and again at 24° C., and 19·974 c.c. were used in the one case and 20·036 c.c. in the other (both of which exactly represent 20 c.c. normal sulphuric acid at 17·5° C.), and no correction had been made for the temperature, the two determinations would then show a difference of—

$$\frac{100(20·036 − 19·974)}{19·974} = 0·31 \text{ per cent.}$$

ε. *Errors which may be caused by the Adhesion of the Liquids to the sides of the containing Glass Vessels.*—These must be taken into consideration, both in the marking and in the use of the measuring vessels. Measuring flasks, for instance, must be marked for their actual contents, burettes and pipettes, however, for the solution as run out ; that is to say, in such a way that the solution as run out shall correspond with the value shown by the division. Some of the solution will still remain, however, attached to the glass sides, the quantity being dependent on the degree of fluidity and adhesion of the liquid. This, with adequate time allowed, drains together again, so that, when titrating, one should wait about two minutes between every reading. In the case of pipettes, the quantity of solution that flows out is most constant when the point of the pipette is placed in contact with the side of the vessel, and subsequently wiped off on it.

| Temp. of the pipette and of the normal solution. | Plus or Minus quantity in thousandths which flowed from the pipette. | | Quantity in thousandths, according to the difference in the expansion of the normal solution and of glass. | Gay-Lussac corr. |
|---|---|---|---|---|
| | I. | II. | | |
| 5° C. | +0·55 | +0·57 | +0·725 | +0·1 |
| 10° | +0·40 | +0·44 | +0·500 | +0·2 |
| 15° | 0 | 0 | 0 | 0 |
| 20° | −0·70 | −0·72 | −0·750 | −0·6 |
| 25° | −1·74 | −1·75 | −1·775 | −1·6 |

In addition to these sources of error, the temperature also influences the quantity of solution that will flow out, as is shown by the accompanying short table given by Mulder (*Die Silberprobirmethode*).

(To be continued).

ZIRCONIUM TETRAIODIDE.

By L. M. DENNIS and A. E. SPENCER.

WITH the exception of the tetraiodide all of the normal halides of zirconium have been prepared and described, the fluoride, chloride, and bromide being white, crystalline, sublimable solids.

A few attempts to make the iodide are recorded in the journals, but in no case was the normal compound, zirconium tetraiodide, $ZrI_4$, obtained. Melliss (*Zeitsch. Chem.*, 1870, 296 ; *Jsb.*, 1870, 328) passed the vapour of iodine over a glowing mixture of zirconia and carbon ; he also treated zirconium tetrabromide with potassium iodide, but in neither case did zirconium tetrachloride result. Hinsberg (*Ann. Chem.*, Liebig, ccxxxix., 253) added an aqueous solution of barium iodide to a solution of zirconium sulphate, filtered off the barium sulphate, and evaporated the filtrate over concentrated sulphuric acid. He obtained a compound of the formula $Zr_2I_3O_3$, or $ZrI(OH)_3$. He also passed the vapour of iodine over a heated mixture of zirconium dioxide and carbon, and states that no reaction whatever took place. Bailey (CHEM. NEWS, lx., 8) states that " zirconium* is acted upon by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained."

In the work here to be described the authors first attempted to prepare zirconium tetraiodide by passing the vapour of iodine over heated zirconium. The zirconium first used was made by reducing zirconium dioxide with magnesium powder, the two substances being mixed in the proportion employed by Winkler (*Ber. d. Chem. Ges.*, xxiii., 2664 ; xxiv., 888) and demanded by the equation—

$$ZrO_2 + 2Mg = Zr + 2MgO.$$
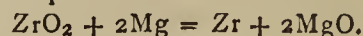
This mixture was heated in hydrogen in the usual manner, and the resulting black powder was removed from the boat, thoroughly ground, and again heated in

* Prepared by the reduction of zirconia with magnesium powder.

hydrogen to insure complete reduction. To free it from magnesia, the product was treated with a saturated solution of ammonium chloride. During this treatment a gas of very disagreeable odour was evolved. It is doubtless similar to that observed by Winkler at this point. The powder was then warmed with dilute 12 per cent hydrochloric acid, and, after collecting it on a filter, it was washed with water containing hydrochloric acid, then with alcohol and ether, and finally was dried in a current of hydrogen. The analysis gave—

|  | | | | Per cent. |
|---|---|---|---|---|
| Zirconium | .. | .. | .. | 80·670 |
| Silicon.. | .. | .. | .. | 0·807 |
| Magnesium | | .. | .. | 0·117 |
| Hydrogen | .. | .. | .. | 0·362 |
| Oxygen (diff.) | .. | .. | 18·044 |
|  | | | | 100·000 |

These results agree quite closely with those obtained by Winkler (*Ber. d. Chem. Ges.*, xxiii., 2667), and indicate that the product of the reduction is chiefly zirconium monoxide rather than zirconium.

Although the powder probably contained but very little free zirconium, it was nevertheless heated in hydrogen, and vapour of iodine was passed over it. An examination of the product gave no satisfactory indications, however, that an iodide of zirconium had been formed.

Inasmuch as the failure to obtain union between the zirconium and iodine might reasonably be ascribed to absence of free zirconium in the above product, it seemed advisable, before attempting any modification of the iodine treatment, to prepare zirconium by some other method and especially by some procedure in which the presence of any appreciable amount of oxygen is avoided. Under the circumstances the method of Berzelius (*Ann. der Phys.*, Pogg., iv., 117), the reduction of potassium fluozirconate with metallic potassium, seemed the most promising, and was therefore employed.

The potassium fluozirconate was prepared from zircon. The zircon was finely ground, sifted through bolting cloth, and digested with concentrated hydrochloric acid until the acid gave no reaction for iron. The powdered zircon, which was now almost perfectly white, was dried and mixed with four times its weight of sodium carbonate. The mixture was fused in an assay crucible furnace, allowed to cool, pulverised, and repeatedly extracted with water. The residue, consisting of zirconia and unattacked zircon, together with some silica and ferric oxide, was heated with concentrated hydrochloric acid, evaporated to dryness, and heated in an air bath to 120° to render the silica insoluble. The dried mass was treated with a little hydrochloric acid, water was added, and the silica and other insoluble matter was filtered off. The filtrate, now containing zirconium chloride and some ferric chloride, was largely diluted with water, and ammonium hydroxide was added until there was formed a slight but permanent precipitate, which was then dissolved by adding as little hydrochloric acid as possible. Sulphur dioxide was then passed into the solution until the liquid smelled strongly of the gas. In many cases a precipitate of basic zirconium sulphite formed at once, but, as the compound seemed to be somewhat soluble in an excess of sulphurous acid, the solution was always boiled for from ten to fifteen minutes to insure complete precipitation. In the reaction free hydrochloric acid is formed, both by the conversion of the zirconium chloride into the basic sulphite and by the reduction of the ferric chloride to the ferrous salt. As this acid would dissolve the zirconium sulphite, it was partially neutralised by the addition, from time to time, of a few drops of dilute ammonium hydroxide. The zirconium precipitate not being wholly free from iron, it was dissolved in hydrochloric acid and again precipitated with sulphur dioxide. The pure zirconium basic sulphite thus obtained was dissolved in hydrochloric acid, and zirconium hydroxide was preci-

pitated by adding ammonium hydroxide. The well-washed hydroxide was dissolved in hydrofluoric acid, potassium fluoride was added, and the resulting potassium fluozirconate was dissolved in hot water and re-crystallised.

The potassium fluozirconate thus prepared was reduced with metallic sodium, the operation being carried out in a cast-iron crucible. The crucible is cylindrical in form, with an internal diameter of 2 inches and depth of 5 inches. The wall and bottom are over 1 inch in thickness. At the top it has a flange 7 inches in diameter, and is provided with a cast-iron cover 1 inch in thickness, which can be firmly fastened to the flange by means of six one-half inch bolts.

In charging the crucible, sodium chloride, finely ground and thoroughly dried, was first put in to the depth of about an inch and a half, and this was then well pounded down with a wooden plunger to compact the salt and expel the enclosed air. On top of the salt were placed alternate layers of potassium fluozirconate, also thoroughly dried, and metallic sodium, these being pounded down as before. The remaining space in the crucible was then filled with sodium chloride, and, after pounding this down, the top was bolted on and the crucible was heated for about three hours with three triple burners. This heat, however, was not sufficient to raise the crucible to redness.

The crucible was then allowed to cool, and, upon opening it, the charge was found to be so compact that it had to be loosened with a chisel. On treating the mass with water, the metallic zirconium, together with a small amount of the oxide which had formed, settled to the bottom, while the sodium chloride and potassium and sodium fluorides dissolved.

The zirconium and zirconium oxide were separated by first floating off the lighter zirconium with water, and then digesting it with dilute hydrochloric acid at 40° until all of the oxide had been dissolved. The resulting product was a black amorphous powder, which, after washing with water, alcohol, and then with ether, showed no trace of impurity before the spectroscope except a slight amount of sodium.

Vapour of iodine was passed over some of this zirconium heated to dull redness in a current of hydrogen, but with no better success than with the other sample. We then concluded to substitute hydriodic acid gas for the iodine. Considerable difficulty was encountered in finding a suitable method of preparing the gaseous hydriodic acid. That described by Merz and Holzmann (*Ber. d. Chem. Ges.*, xxii., 867) was finally found to answer admirably. It consists in passing dry hydrogen and vapour of iodine through a red-hot tube filled with pumice-stone and freeing the hydriodic acid gas from iodine by passing the gases through cotton.

In treating the zirconium with hydriodic acid gas the following apparatus was used:—

Iodine was placed in a small tubulated flask connected on one side with an apparatus furnishing pure dry hydrogen, and on the other side with a long piece of combustion tubing. The half of this tube nearest the iodine flask was filled with pieces of pumice-stone, and rested in a combustion furnace. The other half, extending beyond the combustion furnace, was filled with cotton. The end of this tube was connected with another combustion-tube resting in a second combustion furnace. The porcelain boat containing the zirconium was placed in this second tube.

The hydrogen was first passed through the whole apparatus for several hours, and then the first furnace was lighted. When the pumice had become red hot the flask containing the iodine was gently heated. The tube containing the zirconium soon became filled with the hydriodic acid gas, whereupon the second furnace was lighted. As the temperature rose, a brownish yellow substance collected in the cold end of the combustion-tube, but as the heat became greater the colour entirely

disappeared, and there remained an amorphous white sublimate. No further sublimate was formed until the tube had almost reached a bright red heat, when there appeared, just beyond the point where the tube was red hot, a white crystalline sublimate, different in appearance from that which first formed. The gas escaping from the end of the tube contained hydriodic acid, hydrogen, some iodine, and a trace of iron, the last probably being present in traces in the zirconium and volatilising as ferrous iodide. The tube was kept at a bright red heat for from three to four hours. The gas was then turned off, and when the boat had cooled considerably the heating of the iodine flask was discontinued. The first furnace was then shut off, and the whole apparatus was allowed to cool in the current of hydrogen.

The material in the boat had changed from a black to a greyish white colour, but a chemical examination showed that it contained very little iodine. The amorphous sublimate which first formed was found not to be zirconium iodide, but to contain chiefly iron and iodine.

The crystalline sublimate which was formed only at a red heat was next analysed. These crystals were found to be insoluble in water, nitric acid, hydrochloric acid, aqua regia, and carbon disulphide. They were decomposed and dissolved by concentrated sulphuric acid; they were also decomposed, but not completely, by concentrated nitric acid, iodide being liberated, and a white powder—insoluble in the nitric acid—remaining. This residue was soluble in concentrated sulphuric acid, and from this solution ammonium hydroxide threw down a white gelatinous precipitate. Upon dissolving this precipitate in hydrochloric acid and dipping turmeric paper into the solution, the orange colour characteristic of zirconium was obtained. The solution gave no reaction for iron.

The zirconium in the compound was quantitatively determined by expelling the iodine by heating a portion of the salt with a mixture of sulphuric, nitric, and nitrous acids, dissolving the residue in concentrated sulphuric acid, diluting with water, and precipitating the zirconium with ammonium hydroxide. The precipitate was washed, dried, and ignited, and the zirconium weighed as the dioxide.

The iodine was determined by fusing some of the compound with about five times its weight of a mixture of potassium and sodium carbonate. The mass was then treated with water, filtered, and after acidifying the filtrate with nitric acid the hydriodic acid was precipitated with silver nitrate and weighed as silver iodide.

The results were—

| | Calculated for $ZrI_4$. Per cent. | Per cent. | Found. Per cent. | Per cent. |
|---|---|---|---|---|
| Zirconium | 15·15 | 15·17 | 15·00 | 15·37 |
| Iodine | 84·85 | 85·34 | 85·27 | — |

The crystals when examined under the microscope proved to be clear, colourless cubes, which showed no double refraction.

When heated for some hours in hydrogen the zirconium tetraiodide becomes black, and iodine and hydriodic acid are formed. Heated in the air the iodide melts and sublimes. A weighed amount was placed in a porcelain crucible, covered with water, and evaporated to dryness. No change in weight, and scarcely any in colour, resulted after two such treatments. This behaviour toward water is surprising, for, from the published descriptions of zirconium tetrachloride and tetrabromide, it was to be expected that the iodide would prove to be a hygroscopic compound easily decomposed by water. It seems, however, to more nearly resemble the fluoride which Deville states to be a colourless crystalline substance, volatile at a white heat, and insoluble in water or acids.—*Journal of the American Chemical Society*, vol. xviii., No. 8.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.
*Ordinary Meeting, June 18th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Continued from p. 96).

83. "*On the Colouring-matter contained in the Bark of Myrica nagi.*" By A. G. PERKIN and J. J. HUMMEL.

*Myrica nagi* is an evergreen tree, belonging to the Myriceæ occurring in the sub-tropical Himalayas, in the Khasia mountains, the Malay Islands, and Japan. The bark, which is used as a tanning agent, and occasionally for medicinal purposes, was found to contain a yellow colouring-matter. This formed yellow needles, closely resembling quercetin, having the formula $C_{15}H_{10}O_8$, and yielding compounds with mineral acids, $C_{15}H_{10}O_8H_2SO_4$, $C_{15}H_{10}O_8HBr$, $C_{15}H_{10}O_8HCl$, and $C_{15}H_{10}O_8 \cdot HI$, orange to orange-red needles, decomposed by water into the free acid and colouring matter. In strong solutions of alkali it dissolves with an orange colour, which, on dilution and exposure to air, becomes first green, then deep blue, and finally red-violet. It dyes shades which, in their general character, closely resemble those produced by quercetin and fisetin. The acetyl derivative, $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, m. p. 203—204°, and the benzoyl compound, $C_{15}H_4O_8(C_7H_5O)_6$, m. p. 233—236°, are described. With fused alkali it yields *phloroglucol* and *gallic acid*, and with bromine a compound (orange-brown needles, m. p. 235—240°), the analytical numbers for which agree with the formula $C_{15}H_6O_8Br_4$. This is probably a tetrabromo-derivative of the colouring-matter, but on account of its somewhat peculiar properties, it will require further examination. The results of this investigation show that this colouring-matter, for which the name *myricetin* is proposed, is most probably an hydroxyquercetin,—
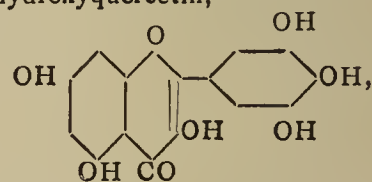


and experiments with its alkyl ethers will be carried out to confirm this point. Its colour reactions with dilute alkali are probably due to the oxidation of the pyrogallol nucleus it contains. The amount of colouring-matter, isolated by the method described, varied from 0·23 to 0·27 per cent, and the amount of tannin it contained, estimated under the direction of Mr. H. H. Procter, Lecturer on Leather Industries, Yorkshire College, was found to be 27·30 per cent.

84. "*Preliminary Note on a New Base derived from Camphoroxime.*" By MARTIN O. FORSTER, Ph.D.

Camphoroxime undergoes no change when treated with boiling methylic iodide in a reflux apparatus, but on heating it with this agent in sealed tubes at 170—180°, the hydriodide of a new base is produced, along with campholenonitrile. The quantity of the salt obtained from 15 grms. of camphoroxime and 30 grms. of methylic iodide was 9·5 grms.

The *base* is a colourless limpid oil, having the odour of piperidine; it boils at 206—207°, and is markedly lævorotatory. It is tertiary in character, and analysis points to the formula $C_{12}H_{19}N$ as representing its composition. (Found: C = 81·06; H = 10·66. Calculated for $C_{12}H_{19}N$, C = 81·35; H = 10·73 per cent).

The *platinichloride*, $(C_{12}H_{20}N)_2PtCl_6$, crystallises from alcohol in magnificent orange needles, and melts, decomposing at 214·5°; the *hydriodide*, $C_{12}H_{19}N,HI$, separates from water in lustrous straw-yellow six-sided plates, and

effervesces vigorously when heated at 285°. The *picrate* and *mercurichloride* are well-defined salts, melting at 190° and 126—128° respectively, whilst the *chromate* crystallises in microscopic pale brown square plates, becoming purple on exposure to light. Incidentally, the *hydrobromide*, and the *acetyl* and *methyl* derivatives of camphoroxime have been obtained.

85. "*The Rotation of Aspartic Acid.*" By B. M. C. MARSHALL, A.R.C.S.

In view of the contradictory statements concerning the rotation of aspartic acid in aqueous solution, the author has re-examined the subject.

Landolt (*Ber.*, xiii., 2334) and Becker (*Ber.*, xiv., 1035) obtained a *lævo*-rotation for aspartic acid, prepared from ordinary asparagine. Piutti (*Ber.*, xix., 1691), on the other hand, states that ordinary asparagine yields *dextro*-aspartic acid, which is convertible into ordinary *lævo*-malic acid, while the *dextro*-asparagine yields *lævo*-aspartic acid, which gives dextro-malic acid.

The results obtained by the author confirm the observations of Piutti. The solubility of the aspartic acid in water was found to be in agreement with the results of Pasteur, Guareschi (*Jahresber.*, 1876, 777), and Engel (*Compt. Rend.*, cvi., 1736), and to be much less than that deduced from Becker's data.

86. "*Synthesis of Pentacarbon Rings. Part III. Condensation of Benzil with Lævulic Acid.*" By FRANCIS R. JAPP, F.R.S., and T. S. MURRAY, D.Sc.

When benzil and lævulic acid are heated with a solution of caustic potash in dilute alcohol, they condense to form two isomeric compounds.

$$C_6H_5 \cdot C(OH) \cdot CH_2 \diagdown$$
$$| \qquad\qquad\qquad CO$$
$$C_6H_5 \cdot C \text{———} C \diagup CH_2 \cdot COOH$$

α-Anhydrobenzillævulic acid (m. p. 187—189°).

and—

$$C_6H_5 \cdot C \text{———} CH \diagdown$$
$$| \qquad\qquad\qquad CO$$
$$C_6H_5 \cdot C(OH) \cdot CH \diagup CH_2COOH$$

β-Anhydrobenzillævulic acid (known only in its salts).
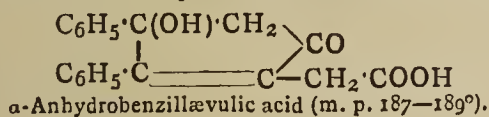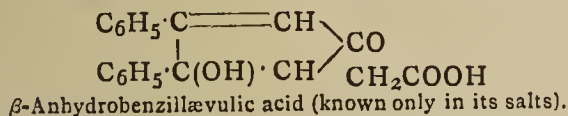
These two *diphenylhydroxycyclopentenonylacetic acids* are allied to anhydracetonebenzil, which is a *diphenylhydroxycyclopentenone* (Japp and Lauder, *Proc. Chem. Soc.*, 1896, 107). The α-acid is stable; the β-acid, when liberated from its salts, spontaneously changes into the lactone,—

$$C_6H_5 \cdot C : CH \diagdown$$
$$| \qquad\qquad\qquad CO$$
$$C_6H_5 \cdot C \cdot CH \diagdown$$
$$| \qquad\qquad\qquad CH_2$$
$$O \cdot CO \diagup$$
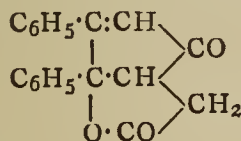
(m. p. 151—152°).

Both the α-acid and the lactone of the β-acid, when boiled for from one to two minutes with fuming hydriodic acid, are converted into *diphenylcyclopentenonylacetic acid*,—

$$C_6H_5 \cdot C \cdot CH_2 \diagdown$$
$$|| \qquad\qquad\qquad CO$$
$$C_6H_5 \cdot C \cdot CH \text{—} CH_2 \cdot COH$$
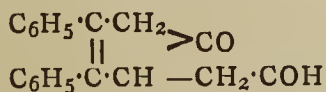
(m. p. 126—127°), a change in the position of the double bonds occurring during the process. The latter acid, on oxidation with sodium hypobromite, yields a mixture of *diphenylmaleic* and *diphenylfumaric acids*.

Oximes and other derivatives of the foregoing compounds have also been prepared.

87. "*Absorption of Dilute Acids by Silk.*" By JAMES WALKER and JAMES R. APPLEYARD.

When silk is dyed with picric acid a real equilibrium is attained which is independent of the original distribution of the materials. If the equilibrium concentration of the picric acid in the silk be denoted by $s$, and in the water by $w$, the relation—

$$s / \sqrt[n]{w} = \text{const.}$$

exists between these magnitudes. This formula would indicate, according to the solid solution theory of dyeing, that the weight of the molecule of picric acid dissolved in the water would be $n$ times that of the molecule of picric acid "dissolved" in the silk; but this we know to be incorrect, as $n$ is greater than unity, and the molecular weight of picric acid in water is the smallest consistent with its formula.

When other solvents than water are used the rate and amount of dyeing with picric acid seem to be connected with the dissociative power of the solvent. Silk will not take up picric acid from benzene or from carbon tetrachloride, but does so readily from alcohol, less readily from ether and acetone. The ratio of the final concentrations of aqueous and alcoholic solutions of picric acid required to dye silk to a given standard was found to be approximately the ratio of the solubilities of picric acid in water and in alcohol.

A comparison of the extents to which the various acids are absorbed by silk shows that the acids fall into two classes—the aromatic acids where the absorption is great, and the non-aromatic acids where the absorption is relatively small. In each class there is a rough parallelism between the strength of the acids and the amount absorbed. The addition of calcium benzoate to a solution of benzoic acid greatly diminishes the strength of the acid, and the absorption also is thereby much diminished.

If dyeing were a pure chemical addition of the dye to the fibre, the theory of mass-action predicts that the equilibrium concentration of the dye-bath should be constant at any given temperature independently of the quantities of material taken. This is not known to be the case for actual dyeing, but it was experimentally verified by "dyeing" diphenylamine brown with picric acid from aqueous solution.

88. "*Position-isomerism and Optical Activity; the Methylic and Ethylic Salts of Ortho-, Meta-, and Para-ditoluyltartaric Acid.*" By PERCY FRANKLAND, Ph.D., F.R.S., and FREDERICK MALCOLM WHARTON, A.I.C.

The authors have commenced the systematic study of the connection between position-isomerism and rotatory power in optically active substances containing the benzene ring. The present paper contains an account of the preparation and properties of the methylic and ethylic salts of the three isomeric ditoluyltartaric acids. These substances were obtained by the action of the three toluyl chlorides on methylic and ethylic tartrates respectively. With the exception of the ethylic salts of the diortho- and dimeta-toluyltartaric acids, they were all obtained as beautifully crystalline bodies, the two ethylic salts in question only as viscid liquids. All six compounds are powerfully lævorotatory, the methylic salts more so than the corresponding ethylic ones, and the para-compounds have the highest, the ortho- the lowest, and the meta- an intermediate rotation. As regards other physical properties, in the case of the methyl compounds, all of which are solids at the ordinary temperature, the para- also has the highest, the ortho- the lowest, and the meta-compound an intermediate melting-point, whilst the density is distinctly greatest in the case of the ortho-compounds, the meta- and para-compounds having almost exactly equal densities. In all cases the rotatory power was determined in the liquid state, no use being made of solutions, and the rotations were compared over wide ranges of temperature. With rise in temperature the lævorotatory power is in all cases diminished, and since the lævorotation is conditioned by the presence of the aromatic groups (methylic and ethylic tartrates being dextrorotatory), the dominant influence of these groups is reduced with increasing temperature; a perfectly analogous phenomenon has already been shown by one of the authors to take place in the case of the dibenzoylglycerates (*Trans.*, 1896, 106). Moreover, as the lævorotation is conditioned by the toluyl groups, it follows from a comparison of the rotations of the compounds described that the meta-toluyl

group has a higher rotatory value than the ortho-, and the para- an even higher one than the meta-.

89. "*Double Sulphides of Gold and other Metals, or the Action at a Red Heat of Sulphur upon Gold when Alloyed with other Metals.*" By J. S. MACLAURIN, B.Sc., University College, Auckland, New Zealand.

It is shown that when alloyed with silver, lead, copper, or iron, gold is readily converted into a sulphide by the action of sulphur vapour on the melted alloys. Analyses of the compounds so prepared are given which prove that the gold sulphide has the formula $Au_2S$.

90. "*The Relative Weights of Gold and Silver dissolved by Potassium Cyanide Solutions from Alloys of these Metals.*" By J. S. MACLAURIN, B.Sc.

The author finds that gold and silver are dissolved by solution of potassium cyanide from an alloy of these metals in the proportions by weight in which they exist in it. He shows that this is the ratio of their atomic volumes, and deduces it from the results previously obtained by him (*Trans.*, 1895, 199).

91. "*The Three Chlorobenzeneazosalicylic Acids.*" By J. T. HEWITT, Ph.D., and H. E. STEVENSON.
*Orthochlorobenzeneazosalicylic acid,*—

$$C_6H_4—(1)Cl(2)—N:N—(4)C_6H_3—(2)CO_2H(1)OH,$$
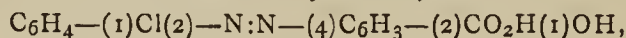
prepared by the addition of diazotised orthochloraniline hydrochloride to an alkaline solution of salicylic acid, forms yellow or buff aggregates of small crystals (m. p. 194°).

Besides metallic salts, the methyl and ethyl esters are described. *Methyl orthochlorobenzeneazosalicylate*, m. p. 109°. *Ethyl orthochlorobenzeneazosalicylate*, m. p. 90—96°.

Attempts to remove hydrochloric acid by inorganic bases were fruitless, and dipheneleneazo derivatives were not produced,

Boiled with aniline, in a flask provided with a reflux tube, a sublimate of ammonium chloride was observed, the chief product of the reaction being a substance of the formula $C_{25}H_{17}N_3O_2$. To effect its isolation, the contents of the flask are freed from aniline by steam distillation, subsequent treatment with soda removes an acid probably having the formula $C_{19}H_{12}N_2O_3$; after washing with hydrochloric acid, the residue is dissolved in chloroform and precipitated by ligroin as a violet crystalline powder.

The formation of the substance $C_{25}H_{17}N_3O_2$ may be thus represented:—

$$C_{13}H_9ClN_2O_3 + 2C_6H_5NH_2 =$$
$$= C_{25}H_{17}N_3O_2 + NH_4Cl + H_2O.$$
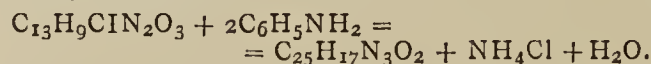
The substance possesses neutral properties, and is probably the anilide of a benzeneindulonecarboxylic acid,—

$$C_6H_4\begin{array}{c}N\\N\end{array}C_6H_3\begin{array}{c}CONHC_6H_5\\O\end{array}.$$
$$|$$
$$C_6H_5$$

*Metachlorobenzeneazosalicylic acid,*—

$$C_6H_4—(1)Cl—(3)N:N—(4)C_6H_3—(2)CO_2H(1)OH,$$
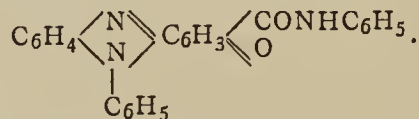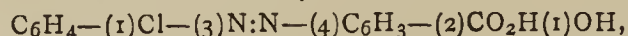
has been previously described (*Ber.*, 1894, xxviii., 803). An account is now given of some of its metallic salts. *Methyl metachlorobenzeneazosalicylate* forms yellow needles which melt at 114°. *Ethyl metachlorobenzeneazosalicylate*, m. p. 102—103°. *Parachlorobenzeneazosalicylic acid*, $C_6H_4—(1)Cl—(4)N:N—(4)C_6H_3—(2)CO_2H(1)OH$, was prepared in the usual manner; it melts at 237°. The *potassium, ammonium, silver,* and *barium* salts are described. *Methyl parachlorobenzeneazosalicylate*, m. p. 152°. *Ethyl parachlorobenzeneazosalicylate*, m. p. 113°.

For purposes of comparison the methyl and ethyl esters of benzeneazosalicylic acid (Stebbins, *Ber.*, 1880, xiii., 716) have also been prepared. *Methylbenzeneazosalicylate*, m. p. 106°. *Ethylbenzeneazosalicylate.* m. p. 88—89°.

92. "*Condensation of Chloral with Resorcinol.*" By J. T. HEWITT, M.A., D.Sc., Ph.D., and F. G. POPE.

H. Causse studied the condensation of chloral with resorcinol in dilute aqueous solution under the influence of sodium hydrogen sulphate (*Bull. Soc. Chim.*, [3], iii., 861—867), In this manner he obtained a colourless compound of the formula $C_{14}H_{12}O_6$; whilst working with hot solutions, yellow crystals of the formula $C_{14}H_{10}O_5$ were obtained. He assigned to these two substances the following constitutional formulæ:—

$$(C_6H_4(OH)O)_2CH \cdot COOH$$

and—

$$\begin{array}{c}C_6H_4(OH)O\\C_6H_4\end{array}\begin{array}{c}\\O\end{array}>CH \cdot CO.$$
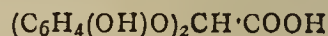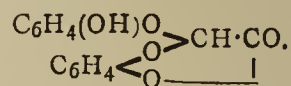
The authors of the present communication have studied the latter substance, and find that it furnishes a triacetyl derivative (m. p. 152°) crystallising in glittering leaflets. The substance $C_{14}H_{10}O_5$ dissolves in cold alkalies with an intense purple colour which disappears on warming, salts of the type $M \cdot C_{14}H_{11}O_6$ being produced. The purple alkaline solution of the formula $C_{14}H_{10}O_5$ gives a precipitate on acidification, solutions of salts $M \cdot C_{14}H_{11}O_6$ only on boiling for some time.

The conclusion can be drawn that the compound $C_{14}HO_5$ is the lactone of an acid, $C_{14}H_{12}O_6$, which is itself readily soluble in water. This acid must contain four hydroxyl groups, and is, therefore, *tetrahydroxydiphenylacetic acid.*

Probably the acid and lactone possess the following constitutional formulæ:—

$$CH\begin{array}{c}(1)C_6H_3<\begin{array}{c}(2)OH\\(4)OH\end{array}\\(1)C_6H_3<\begin{array}{c}(4)\\(2)OH\end{array}\end{array} \quad and \quad CH\begin{array}{c}(1)C_6H_3<\begin{array}{c}(2)OH\\(4)OH\end{array}\\(1)C_6H_3<\begin{array}{c}(4)OH\\(2)—\end{array}\end{array}$$
$$|$$
$$COOH \qquad\qquad CO——O———$$
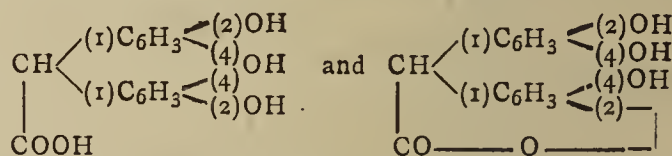
93. "*The Atomic Weight of Japanese Tellurium.*" By MASUMI CHIKASHIGÉ, B.Sc., Imperial University, Japan.

A re-determination of the atomic weight of tellurium has been made by means of its tetrabromide, and by closely following Brauner in all the details. The result has been to get, in the three experiments made, the numbers 127·57, 127 61, and 127·58, which, therefore, agree with his in making the atomic weight 127·6. This work was undertaken by the advice of Dr. Divers, in order to ascertain whether tellurium found under mineralogical conditions quite unlike those pertaining to the tellurium employed by Brauner, Staudenmaier, and all others who have investigated the subject, has the same atomic weight as the latter. That, as is well known, occurs in Hungary and elsewhere, in union with bismuth, gold, silver, &c., while the tellurium employed in this research was obtained from the *red* native sulphur, or telluro-sulphur, of Japan, discovered and described in 1883 by Divers, Shimosé, and Shimidzu. It is extremely improbable that, if the substance known as tellurium is compound, as it has been considered to be by Brauner, its composition should be identical when occurring in association with sulphur as a sulphur-like body in Japan, as when occurring in metallic combination in Europe or America. Since Staudenmaier has got the same atomic weight for tellurium of European origin as that found by Brauner, but by a totally different method, and that the author has again got the same atomic weight by Brauner's process, but working on a tellurium of quite dissimilar origin, the point may be regarded as settled that its atomic weight exceeds that of iodine. Its occurrence with sulphur and selenium in the Japanese mineral at the same time furnishes additional proof that it belongs to the sulphur group.

ADDENDUM, BY EDWARD DIVERS.—The case of tellurium and iodine, with atomic weights in the reverse order of their places in the periodic series, is not the only one. Cobalt belongs, undoubtedly to the second division of

Group VIII., and nickel to the third division, according to both Mendeleeff and Lothar Meyer; yet all the elaborate work done on the subject has left cobalt with an atomic weight slightly higher than, or at least equal to, that of nickel. Hence we find in most books cobalt and nickel misplaced in the reproduction of Mendeleeff or Meyer's table. It is to be hoped no one will venture now to misplace tellurium and iodine.

94. "*Derivatives of Camphene Sulphonic Acids.*" By ARTHUR LAPWORTH and FREDERIC STANLEY KIPPING.

The two chlorocamphenesulphonic chlorides obtained as by-products in the sulphonation of camphor (compare *Proc.*, 1895, 57) have been submitted to a further examination. Although no experimental proof of their relationship to camphene has yet been obtained, their characterisation has now been completed, and a number of new derivatives have been prepared from them.

*α-Chlorocamphene sulphochloride*, $C_{10}H_{14}Cl \cdot SO_2Cl$, is dimorphous, as was at first expected (*loc. cit.*). It crystallises from light petroleum or cold methylic alcohol in massive transparent anorthic prisms or plates, which melt at 83—84°; from hot methylic alcohol it is deposited in small orthorhombic tables which melt at 87—88°. The latter modification is also obtained when the melted substance is quickly cooled, and undergoes gradual reversion to the anorthic modification at the ordinary temperature. Both forms have been goniometrically measured.

*α-Chlorocamphene sulphanilide*,—

$$C_{10}H_{14}Cl \cdot SO_2 \cdot NHC_6H_5,$$
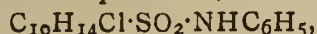
crystallises in small flattened needles, which probably belong to the anorthic system; it is readily soluble in alcohol, but only sparingly soluble in ether or chloroform; it melts and decomposes about 232—234°.

*α-Chlorocamphene sulphonic acid*, $C_{10}H_{14}Cl \cdot SO_3H$, crystallises from ether in beautiful glistening elongated plates; it dissolves sparingly in ether and in chloroform, but is insoluble in petroleum. When heated it gradually darkens, and at 264—265° swells up and evolves gases, finally forming a dark-coloured liquid mass.

*β-Chlorocamphene sulphochloride*, $C_{10}H_{14}Cl \cdot SO_2Cl$, crystallises from anhydrous methylic alcohol in long needles which belong to the tetragonal system, and melts at 83—84°; the low melting-point (78°) originally observed was probably due to some slight admixture with the isomeric sulphochloride, the latter being almost impossible to eliminate by crystallisation from petroleum.

*β-Chlorocamphene sulphanilide*, $C_{10}H_{14}Cl \cdot SO_2 \cdot NHC_6H_5$, is slightly soluble in hot water, and crystallises from dilute alcohol in branched aggregates of plates; it melts at 101—103°.

*β-Chlorocamphene sulphonic acid*, $C_{10}H_{14}Cl \cdot SO_3H$, is readily soluble in water, and crystallises from ether in minute ill-defined leaflets; it melts at 73—74°, and decomposes and evolves gases at about 142°. When the solution of this acid is evaporated to dryness on the water-bath, and the residue extracted with water, a substance remains undissolved which is isomeric with β-chlorocamphene sulphonic acid. This compound crystallises from methylic alcohol in well-defined plates, which aggregate on pressure to a camphor-like mass; it melts at 183·5—184·5. It is not altered by hot aniline, but is gradually dissolved by boiling baryta water, forming an ill-defined salt. Its behaviour is in accordance with the supposition that it is the lactone of a hydroxy-sulphonic acid.

95. "*Iodoso- and Iodoxy-Benzaldehydes.*" By VICTOR MEYER and T. S. PATTERSON.

It is shown that *m*- and *p*-iodoso- and iodoxy-benzaldehydes are much easier to prepare than *o*-iodoso-benzaldehyde, which is contrary to the hitherto observed rule.

The preparation of the following new substances is described:—

*m*-Iodo-benzaldehyde, m. p. 57°. *m*-Iodo-benzaldehyde-bichloride. *m*-Iodoso-benzaldehyde; decomposes (*circa*)

190°. *m*-Iodoso-benzaldehyde-acetate, m. p. 157°. *m*-Iodoxy-benzaldehyde. *p*-Iodo-benzaldehyde-bichloride. *p*-Iodoso-benzaldehyde; decomposes at 115°. *p*-Iodoxy-benzaldehyde; decomposes at 216°. *o*-Iodo-benzaldehyde-bichloride. *o*-Iodoso-benzaldehyde; decomposes at 205—210°. *o*-Iodo-benzaldoxime, m. p. 107—108°. *m*-Iodo-benzaldoxime, m. p. 62—63°. *p*-Iodo-benzaldoxime, m. p. 111°. *o*-Iodo-benzaldehyde-phenylhydrazone, m. p. 79°. *m*-Iodo-benzaldehyde-phenylhydrazone, m. p. 155°. *p*-Iodo-benzaldehyde-phenylhydrazone, m. p. 121°.

96. "*α-Isopropylglutaric Acid.*" By W. H. PERKIN, jun., F.R.S.

During the course of experiments on derivatives of glutaric acid, the author had occasion to carefully study the action of alkalis on ethylic methylisopropyl-α-brom-acetate, and also the action of this ethereal salt on the sodium derivative of ethylic malonate.

$(CH_3)_2 \cdot CH \cdot C(CH_3)Br \cdot COOC_2H_5$, *ethylic methylisopropyl-α-bromacetate*, was prepared by brominating methylisopropylacetic acid in the presence of phosphorus, and pouring the product into alcohol; it boils constantly at 130° (100 m.m.). When heated with quinoline, this ethereal salt yields a mixture of the ethereal salts of α-isopropylacrylic and of trimethylacrylic acids, elimination of hydrogen bromide taking place in two directions, thus:—

$$\text{I.} \quad (CH_3)_2CH \cdot C(CH_3)Br \cdot COOC_2H_5 = \\ = (CH_3)_2CH \cdot C \cdot COO_2H_5 + HBr. \\ \overset{\|}{CH_2}$$

$$\text{II.} \quad Me_2CH \cdot C(Me)Br \cdot COOEt = \\ = Me_2 \cdot C : C(Me) \cdot COOEt + HBr.$$
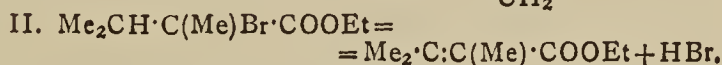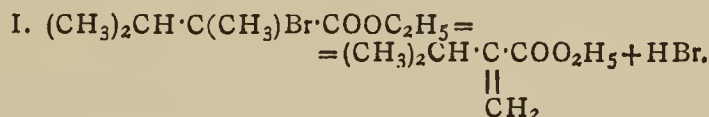
And, when digested with alcoholic potash, the bromo-ethereal salt yields a mixture of the above acrylic acids, together with small quantities of methylisopropyl-α-hydroxyacetic acid.

*Trimethylacrylic acid*, $(CH_3)_2 \cdot C : C(CH_3) \cdot COOH$, crystallises in colourless prisms, and melts at 71°; it combines with bromine, yielding *αβ-dibromotrimethylpropionic acid*, $(CH_3)_2CBr \cdot CBr(CH_3) \cdot COOH$ (m. p. 190°), and with hydrogen bromide and hydrogen iodide with formation of $(CH_3)_2 \cdot CBr \cdot CH(CH_3) \cdot COOH$, *β-bromotrimethylpropionic acid* (m. p. 79°), and $(CH_3)_2 \cdot CI \cdot CH(CH_3) \cdot COOH$, *β-iodo-trimethylpropionic acid* (m. p. 81°) respectively.

*α-Isopropylacrylic acid*,—

$$(CH_3)_2 \cdot CH \cdot C \cdot COOH \\ \overset{\|}{CH_2},$$
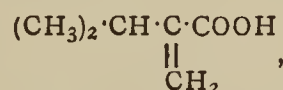
has not been obtained in a pure state.

$(CH_3)_2 \cdot CH \cdot C(OH) \cdot CH_3 \cdot COOH$, *methylisopropyl-α-hydroxyacetic acid*, crystallises in colourless prisms and melts at 75—76°.

*Condensation of Ethylic Isopropylacrylate with the Sodium Compound of Ethylic Malonate.* — When the mixed ethereal salts of isopropylglutaric acid and trimethylglutaric acid (as obtained by the action of quinoline on ethylic methylisopropyl-α-bromacetate) are digested with the sodium derivative of ethylic malonate in alcoholic solution, condensation takes place, curiously enough, only in the case of the former substance.

$$Me_2CH \cdot C : CH_2 + CH_2(COOEt)_2 = \\ \underset{COOEt}{|}$$

$$= \underset{\underset{COOEt \; (COOEt)_2}{| \quad \quad |}}{Me_2 \cdot CH \cdot CH \cdot CH_2 \cdot CH},$$
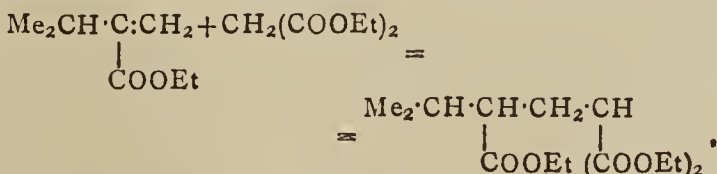
The *ethylic isopropylpropanetricarboxylate* thus formed is a thick colourless oil which boils constantly at 209° (45 m.m.), and, on hydrolysis, yields the corresponding isopropylpropanetricarboxylic acid; this acid melts at 165° with decomposition into $CO_2$ and α-isopropylglutaric acid.

*α-Isopropylglutaric acid,—*

$$(CH_3)_2CH \cdot CH \cdot CH_2 \cdot CH_2$$
$$\underset{COOH}{|} \qquad \underset{COOH}{|},$$
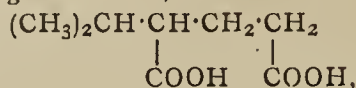
melts at 94—95°, and in its properties shows considerable resemblance to the isomeric—

$$COOH \cdot CH_2 \cdot C(CH_3)_2 \cdot CH(CH_3) \cdot COOH,$$
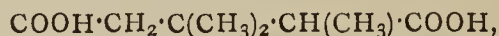
*αββ*-trimethylglutaric acid, which Balbiano (*Ber.*, 1895, xxviii., 1507) obtained from the products of the oxidation of camphoric acid with cold potassium permanganate. It yields an ethereal salt which boils at 158—160° (45 m.m.), an anhydride, $C_8H_{12}O_3$ (m. p. 53°), an anilic acid, $C_{14}H_9NO_3$, which melts at 159°, and it is oxidised by chromic acid with formation of acetic and succinic acids.

*Action of Ethylic Methylisopropyl α-Bromacetate on the Sodium Compound of Ethylic Malonate.*—This reaction was studied under a variety of conditions, using alcohol and xylene as solvents, but in all cases the product was found to be identical with the ethylic isopropylpropanetricarboxylate, obtained, as described above, by the condensation of ethylic isopropylacrylate with the sodium derivative of ethylic malonate. During this reaction the ethylic methylisopropylbromacetate is obviously first converted into ethylic isopropylacrylate, which then condenses with the sodium compound of the ethylic malonate in the manner described above.

(To be continued).

# NOTICES OF BOOKS.

*Commercial Organic Analysis.* A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, &c., with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S., Past President of the Society of Public Analysts, Public Analyst for the West Riding of Yorkshire, the City of Sheffield, &c. Second Edition, Revised and Enlarged. Vol. iii., Part 3. London : J. and A. Churchill. 1896. 8vo., pp. 508.

MR. ALLEN'S *magnum opus* approaches its conclusion, and certainly betrays no signs of deterioration in the quality of its matter. The present volume contains the conclusion of the vegetable alkaloids, the non-basic vegetable bitter principles, the animal bases, the animal acids, and cyanogen with its derivatives.

Among the alkaloids we find carpaine, the basic principle of *Carica papaya*, which is correctly described as a Javanese tree, in contradiction to the common error which makes it a native of South America. It must not be confounded with the ferment papain. Colchicine, dear to the heart of certain quacks, is described, not without a caution as to its poisonous and uncertain effects.

The adulterations of pepper appear to be numerous. In a note we read that the Somerset House chemists allow $3\frac{1}{4}$ per cent of sand, and an additional 7 per cent of mineral matter is stated to be allowed by " public analysts and writers of authority." Mr. Allen pronounces such allowances quite indefensible.

Solanine and solanidine are met with in potatoes which are either unripe or are sprouting. They have been found in the residues of a German distillery, and have poisoned cattle.

The use of chrome-yellow for the sophistication of mustard seems to be a sin of the past. But Martius yellow has been found in mustards of French, German, and American manufacture.

A remarkable fact is that solutions of *digitalis* are poisonons to plants. The *digitalis* poisons occur also in the leaves of the oleander.

Under the heads " Ouabain " and " Antiarin " we find a very interesting survey of the arrow-poisons used by various savage tribes.

It is a curious fact that *Pyrethrum carneum* and *P. roseum* are probably present in " insect-powders," which, by the way, are not harmless to higher animals.

Chirette or chiraytor figures in certain proprietary medicines, and is also used as a substitute for hops.

Full justice is done to the subject of the ptomaines, including the chemistry of putrefaction, which is now understood as a fermentation in nitrogenous organic matters set up in presence of bacteria. It is remarked, on the authority of Brieger, that the formation of a highly toxic ptomaine corresponds with the disappearance of choline. Some of these products of putrefaction—such as cadaverine, putrescine, and saprine—are not poisonous, but nydaleine is a highly poisonous diamine. The typhoid bacillus of Eberth is not produced in putrefaction, but there are found in the excreta of the patients traces of a base which proves rapidly fatal.

The odour of some ptomaines resembles that of syringa, and is so persistent that it has been observed in products of ancient putrefaction, found in bone-caves. But in other cases it is found that these products of putrefaction are most dangerous which do not attract attention by odours or by change of colour or texture.

There is the very suggestive caution laid down that " ptomaines produced by putrefactive decomposition after death have been mistaken for poisonous vegetable bases administered during life."

Mytilotoxine, $C_6H_{15}NO_2$, has been obtained from putrescent mussels, and is supposed to be the agent in mussel poisoning. Brieger's typhotoxine is supposed to be the poison of typhus fever; and tetanine, $C_{13}H_{30}N_2O_4$, is believed, as its name indicates, to be the active agent in tetanus.

Vaughan's tyrotoxicon is obtained from stale milk, ice-creams, and decomposing cheese. It produces symptoms identical with those of *cholera infantum*. It is highly remarkable that cod-liver oil yields two poisonous ptomaines—morrhuine, $C_{19}H_{27}N_3$, and aselline, $C_{25}H_{32}N_4$.

There is a notice of the arsenical ptomaines suspected to have been present in the *Aqua Tofana* and *Acquetta di Perregia* celebrated in the history of mediæval secret poisoning. Husemann suggests that similar compounds may be generated in the size and paste used in fixing arsenious papers on the walls of bed-rooms.

Space unfortunately warns us to curtail our further survey of this most valuable and interesting book, but we cannot refrain from quoting the collapse of prisoner's counsel in the trial of Tawell. The learned advocate suggested that the prussic acid detected in the stomach of the deceased might be derived from apple-pips, and dropped the subject when told that " about a peck " might suffice.

*The Glasgow and West of Scotland Technical College Calendar for the Session* 1896—97. Glasgow : Printed for the College.

THE Glasgow and West of Scotland Technical College reminds us in many respects of the Polytechnicum of Zurich, of Aix-la-Chapelle, &c. It is, however, more contaminated with examinationism, to which we Britons still cling " like a dormant bat to a dead bough," despite its grand break-down, civil and military, in the land where it took its origin.

The College seems to have been formed by the coalescence of what was formerly known as the Andersonian University, the Young Laboratory, and Allan Glen's School.

The Freeland chair of Chemistry is at present filled by Prof. Henderson. It has a junior and a senior course of chemistry, inorganic and organic, all arranged for students preparing for certain experiments here specified. Now the chemical classes at the Aix-la-Chapelle, or the

polytechnics, are adapted simply for students seeking to acquire a sound knowledge of chemical sciece, and we venture to say that they answer the purpose.

The " Freeland " Laboratory is open daily (Saturdays excepted) throughout the academical year, from 9 a.m. to 5 p.m. We are glad to find that there is a special course of demonstration in Spectrum Analysis.

The " Young " chair of Technical Chemistry is filled by Prof. Mills. We do not see whether the students, like the rivals in Germany and Switzerland, have the opportunity afforded them of visiting the different manufacturing establishments which are here referred to. There is a course for the construction and use of chemical plant which should prove highly valuable.

The course of technical organic chemistry, 21 lectures, will begin on Wednesday, October 7th.

Among subsidiary courses is one on dyeing processes, and one on oils, paints, and varnishes, including the conversion of pigments into paints. There is also a special photographic department, and a department for metallurgy and mineralogy conducted by Prof. Sexton.

The scientific principles of agriculture are taught by Prof. Wright in a course of 100 lectures. Agricultural botany is taught by Mr. McAlpine, and economic entomology by Mr. J. F. X. King.

There is also an evening department of the College, in which natural philosophy is taught by Prof. Blyth, chemistry by Prof. Henderson, technical chemistry by Prof. Mills, and agriculture by Prof. Wright. Dr. Barlow lectures on physiology and hygiene.

A course of lectures on music seems to us strangely out of place in an establishment like the Glasgow College. On the Continent, where the study of music is not neglected, it is taught in Conservatoriums, establishments perfectly distinct from the Universities.

In our opinion the Technical College might rival, or even surpass, any foreign Polytechnicum if certain departments were deleted, and if the time and brain-power of the students were not frittered away in preparing for examinations.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 2.

Micro-chemical Distinction between Cinchonidine and Hocinchonidine.—H. Behrens.

General Volumetric Determination of the Metals Precipitable by Fixed Alkalis, Caustic or Carbonated.—Prof. Dr. Ruos.—Already inserted.

Examination of Fine Spirit for the Determination of Fusel Oil.—A. Stutzer and R. Maul.—The procedure employed is an improvement on that of Roscoe. It consists firstly in a concentration of the fusel by eliminating a portion of the alcohol, which must be regarded as free from fusel, or as containing only minimum traces. The next step is to ascertain the specific gravity and dilute the liquid to 30 per cent by volume. The author then gives an account of the apparatus for shaking out with chloroform, of charging the apparatus, and of the manner of shaking out.

Valuation of Benzidin and Toluidin.—W. Vaubel.—Already inserted.

Behaviour of the Naphthols and Naphthylamines with Nascent Bromine.—W. Vaubel.

Peculiar Relations of Solubility in Barium Sulphate.—R. Fresenius and E. Hintz.

Iodine Number and Index of Refraction of Cacao Butter.—Dr. A. Strohl.—The iodine number of pure cacao butters of different origin, degree of ripeness, &c., vary from 32·8 to 41·7. The indices of refraction, determined at 40°, vary from 1·4565 to 1·4578. A cacao butter having a low iodine number will have as a rule a low index of refraction.

Hydrometer Pipette.—Greiner. — This instrument, which is patented, is shown in the figure accompanying the paper.

Process for Dissolving Ignited Iron Oxide and other Metallic Oxides.—Hugo Borntrager.—Already inserted.

Gas Analytical Methods and Apparatus. — W. Fresenius (with the co-operation of W. Schranz.—These include figures and descriptions of the devices of C. Kippenberger, of F. Fischer, G. Neumann, of W. Thörner, of Binder (*Chemiker Zeitung*), of Adeney (CHEMICAL NEWS), of W. Younger (*Journ. Soc. Chem. Industry*), of Wanklyn and Cooper (CHEMICAL NEWS), pronounced useless by L. L. de Koninck (*Zeit. fur Angew. Chemie*) and others.

Determination of the Halogens.—C. Schierholz (*Monatshefte fur Chemie*).

Solubilities of the Silver Haloids in Organic and Inorganic Solvents. — E. Valenta (*Monatshefte fur Chemie*).

Gas-volumetric Determination of Free Iodine.—A. Baumann.—The author shows that his method, above all, requires a rapid mixture of the alkaline solution of hydrogen peroxide with the solution of iodine, in order that the latter may become quickly alkaline in its whole extent, and no higher oxidation of the hypoiodous acid can ensue. According to Baumann's directions, we bring the solution into rotatory movement *before* mixture; incline, then, the generating vessel quickly by about 90°, so that the entire quantity of the alkaline solution of hydrogen peroxide can mix with the solution of hydrogen, and turn the liquid in the slanting position of the glass for about five seconds. If we then shake the entire liquid for ten seconds, the analysis is completed, and the generating apparatus is returned to the cooling water. Every analysis is to be regarded as worthless in which a longer time— say, about one minute—is required for shaking out the gases.

Action of Nascent Bromine upon Benzene.—W. Vaubel (*Journ. Prakt. Chemie*).

Recognition of Indoles and Indol Carbonic Acids.—A. Angeli (*Gazetta Chim. Italiana* and *Journ. Chem. Society*).—The author fuses traces of the substance in a small glass tube with dehydrated oxalic acid. There appears a beautiful colour and the melted product dissolves in acetic acid. Indol and its aliphatic homologues yield a red colouration, whilst with a-phenylindol a violet is produced.

Determination of Chlorine in Organic Products, *e.g.*, in Urine.—G. Meillière (*Journ. Pharm.*).—The author evaporates the substance to dryness with an equal quantity of a 20 per cent solution of calcium nitrate in a platinum capsule. A slight ignition of the residue suffices to destroy the carbonaceous compounds. The watery extract of the residue is free from phosphates. We acidulate slightly with dilute sulphuric acid, and add some calcium carbonate in order to decolourise the liquid. In the neutral colourless filtrate the chlorine can be determined in the usual manner, using potassium chromate as indicator.

Volumetric Determination of Halogens in Organic Substances.—F. W. Küster.—The author, in opposition to J. Walker and J. Henderson (CHEMICAL NEWS), states that he has always obtained inaccurate results with the process of Carius as modified by Volhard. Walker and Henderson now show that a part of the silver nitrate is absorbed by the glass only if the decomposition is effected

at too high a temperature (320—340°), as was done by Küster, and the quantity of fuming nitric acid is too small. For most haloidiferous organic substances it is sufficient to heat the tubes to 250—260° for three hours, taking to 0·1 grm. of the substance 2 c.c. nitric acid of specific gravity 1 5. The action of the excess of silver nitrate is then completely avoided, and the results agree with those obtained by the gravimetric method.

**Elementary Analysis with the Use of Lead Chromate.**—Bruce Warren—From the CHEMICAL NEWS (vol. lxxi., pp. 143, 152).

**Determination of Nitrogen in Nitriferous Manures.** —W. E. Garrigues.—From the CHEMICAL NEWS (vol. lxxi., p. 41).

**Determination of Nitrogen in Arable Soils.**—W. Dafert (*Experimental Station Record* and *Journ. Chem. Society*).—In order to avoid the troublesome bumping of the liquid, the author proposes to effect the distillation of the ammonia produced with the introduction of watery vapour. If the soil contains a large quantity of insoluble constituents, it is well to filter after opening up the specimen with sulphuric acid.

**Determination of Nitric Nitrogen in Presence of Organic Nitrogen.**—Th. Pfeiffer and H. Thurmann (*Land. Versuchsstationen*).

**Determination of Sugars.**—Lasche (*Biedermann's Central Blatt* and *Journ. Chem. Soc.*).

**Determination and Separation of small Quantities of Methylic and Ethylic Alcohols.**—L. Prunier.—From the *Journal of the Chemical Society* and the *Journ. Pharm.*

**Separation of Ethylic Alcohol from Acetic Acid, Methylic Ether, Methyl Acetate, Aldehyds, Phenols, &c.**—Maxime Cair-Mantrand.—From the *Comptes Rendus*.

**Examination of and Conclusion on Wine.**—A number of methods collated by W. Fresenius, assisted by L. Grünhut.

**Examination of Balsam of Peru.**—Otto Schade (*Pharm. Zeitung*).—The author finds that the yellow colouration prescribed as a test by the Pharm. Germanica on shaking up with petroleum benzin, evaporating off the latter substance from the filtrate, and adding a few drops of crude nitric acid, does not in all cases appear. But if the petroleum-ethereal extract, after evaporation, is further heated on the water-bath for ten to twelve minutes, the required yellow colour appears. Gehe and Co. prefer the determination of the cinnamein as proposed by Flückiger.

**Recognition of Fatty Oils in Balsam of Copaiva.**— E. Hirschsohn (*Pharm. Zeitung für Russland*).—Twenty to thirty drops of the balsam in question are covered with 1 to 2 c.c. of a solution of 1 part caustic soda in 5 parts alcohol (at 95 per cent), boiled up several times, and when cold mixed with twice its volume of ether. If oil is present the mixture is gelatinous.

**Contributions to Forensic Chemistry.**—W. Lenz.— The author collates procedures published by Dragendorff for a number of powerful agents. The detection in general is effected according to Dragendorff's general method. The acidulation of the mixture to be submitted to " shaking out " is always effected with dilute sulphuric acid, and alkylisation with ammonia. The substances especially considered are (*a*) the esters of guaiacol, naphthol, cresol, &c., and (*b*) amidic compounds.

**Experiments on the Atomic Weight of Cobalt.**— H. Thiele.—Already inserted.

To this issue there is appended a very complete table for calculating the phosphoric acid in magnesium phosphate. The table gives the corresponding weights of $P_2O_5$ in grms. for all weights of $Mg_2P_2O_7$ from 0·0001 grm. to 0·4000 grm., the coefficient being 0 63964. The calculations have been collated by Dr. Göltschke, of Brunswick.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1919.

## FOURTEENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

THE Committee on Indexing Chemical Literature presents to the Chemical Section its Fourteenth Annual Report.

During the year ending August, 1896, there has been exhibited much activity in chemical bibliography and indexing; several valuable works have been completed and many important undertakings have been begun.

### Works Published.

"A Dictionary of Chemical Solubilities." *Inorganic.* By Arthur Messinger Comey. New York and London, 1896. Pp. xx.—515. 8vo.

Professor Comey is to be complimented on the completion of the first part of his extensive undertaking, and chemists are to be congratulated on the publication in such good form of so important an aid to research. It is to be hoped that this volume will be so well received as to encourage the author to follow promptly with the organic section.

"Index to the Literature of the Detection and Estimation of Fusel Oil in Spirits." By W. D. Bigelow. *Journ. Amer. Chem. Soc.*, vol. xviii., No. 4, p. 397.

This was announced in our report for 1895.

"Bibliography of Embalming," in a Thesis entitled: "Embalming and Embalming Fluids," by Charles W. McCurdy (of the University of Idaho). *Post Graduate and Wooster Quarterly*, April, 1896.

A very full bibliography of this unique subject, which has its chemical aspects as well as its grave ones. It comprises about 500 entries, in several modern languages, arranged alphabetically by authors.

"References to Capillarity," by John Uri Lloyd. In his "Study in Pharmacy." Privately printed. Chicago, 1895—96. 8vo.

"Atomic Weights" form the subject of a brief bibliography (24 titles) accompanying an article on the same topic by Alexander Scott. *Science Progress*, vol i., p. 542 (Aug., 1894).

"The Composition of Water." A short bibliography. By T. C. Warrington. CHEM. NEWS, vol. lxxiii., p. 137 *et seq.* (March, 1896).

"A Short List of Books on Chemistry." Selected and annotated by H. Carrington Bolton. *Scientific American Supplement*, Oct., 19, 1895.

"Bibliography as a Feature of the Chemical Curriculum." By H. Carrington Bolton. *Science*, Oct. 4, 1895.

"Review of American Chemical Research." Edited by Arthur A. Noyes. In the *Technology Quarterly*, issued by the Massachusetts Institute of Technology, Boston, Mass.

The first paper appeared in the number for April, 1895 (vol. viii., p. 90); the reviews consist of abstracts of papers in periodicals, grouped under the following heads: —General and Physical Chemistry, Inorganic, Organic, Technical, Sanitary, Agricultural, Vegetable, Metallurgical, Assaying, Geological, Mineralogical, Apparatus. Each abstract is signed by the abstractor.

This Review promises to be an important contribution to contemporary chemical science of America, and deserves to be well supported.

"Enumeration of Titles of Chemical Papers." This bibliography has been published monthly since May, 1894, in *Science Progress*, London. It embraces titles (without comments) in several European languages.

"Bibliography of Agricultural Chemistry (American)."

The several publications of the scientific bureaus of the United States Government contain many valuable contributions to chemistry in its applications to agriculture and the arts, widely scattered in their pages, and it has been difficult to keep informed with reference to them. Thanks, however, to the excellent bibliographical work of the Office of Experiment Stations, U. S. Department of Agriculture, Washington, D.C., the chemical treatises published in the Bulletins of the State Institutions are made accessible; this is accomplished in the three publications here named:—*Experiment Station Record*, vol. iii., No. 12, July, 1892. *Bulletin*, No. 19 (1894), and *Bulletin*, No. 23 (1895). Organisation Lists of the Agricultural Experiment Stations, U. S. Department of Agriculture, Office of Experiment Stations.

These contain: "Lists of Station Publications," giving dates, bulletin-numbers, and titles of each bulletin, under each State, alphabetically arranged. For the agricultural chemist these bibliographical helps are too important to be overlooked.

The Committee also chronicles the publication of the following valuable aids to chemical research :—

"Synopsis of Current Electrical Literature during 1895." By Max Osterberg. New York (D. van Nostrand Co.), 1896. Pp. xiii.—143. 8vo.

This is a classified index with an index to authors, compiled from fifty-nine foreign and American periodicals; it is intended to be published annually.

"General-Register zu Ladenburg's Handwörterbuch der Chemie." Breslau, 1895. Pp. 160. 8vo.

"Bibliographie des travaux scientifiques" . . . publié par les sociétés savantes de la France, dressés sous les auspices du ministère de l'instruction publique; par J. Deniker. Paris, 1895. 4to.

### Reports of Progress.

The "Index to the Mineral Waters of the World," by Dr. Alfred Tuckerman, noticed in previous reports has been completed and accepted for publication by the Smithsonian Institution.

The manuscript of a new edition of the "Catalogue of Scientific and Technical Periodicals, 1865-1882," by Dr. H. Carrington Bolton, has been completed and is now going through the press. The new edition will be issued by the Smithsonian Institution as a volume of the Miscellaneous Collections. The bibliography includes chemical journals, and is brought down to the year 1895.

Dr. Bolton reports progress on a Supplement to his "Select Bibliography of Chemistry, 1492-1892," the printing of which is, however, postponed.

Professor James Lewis Howe reports the completion of the manuscript of an "Index to the Literature of Platinum and its Compounds"; this will be presented to the Chemical Section at the same session with this report.

Professor F. P. Venable has completed an "Index to the Literature of the Periodic Law." It will accompany his "Development of the Periodic Law," soon to be published by the Chemical Publishing Co., Easton, Pa.

### Works in Preparation.

Dr. Alexis A. Julien has no less than three bibliographical works well advanced:—(1) "A Bibliography of Sand" (including chemical analysis, &c.).

(2) "A Bibliography of Pedesis, or the Brownian Movement."

(3) "A Bibliography of the Condensation of Gases on the Surface of Solids."

Dr. Arthur C. Langmuir is engaged on an "Index to the Literature of Zirconium."

Mr. George Wagner, of the University of Kansas, has undertaken an "Index to the Literature of Oxygen," on a large scale. In this work he will have the counsel of Professor Albert B. Prescott.

Dr. C. H. Joüet has the manuscript of an "Index to the Literature of Thorium" well advanced towards completion.

Professor Rudolf A. Witthaus has compiled a "Bibliography of Forensic Toxicology," which will appear in Vol. IV. of Witthaus and Becker's "Medical Jurisprudence," New York, 1896.

The *Journal of the Society of Chemical Industry* announces a Collective Index for the whole series, 1881—1895. This is to be ready in 1896, and will form a volume of about 500 pages quarto.

Attention is called to a plan for facilitating bibliographical researches, adopted by the American Pharmaceutical Association. The Research Committee of this Association employs a Reference Reader whose duty it is to supply original literature to investigators working in the Committee and with it. A list of the chief serials and a few encyclopædic works is placed in the hands of those who apply for the services of the Reader. Transcripts, abstracts, and translations are supplied. The service is chiefly for literature beyond the smaller libraries, and is under the direction of the Chairman of the Committee.

Perhaps a similar scheme might be organised within the American Association for the Advancement of Science.

In conclusion, the Committee on Indexing Chemical Literature desires to state to those not acquainted with the announcements made in the preceding annual reports that it labours to foster individual undertakings in chemical bibliography, to prevent futile duplication of work, to record in these reports completed bibliographies and new enterprises, as well as to chronicle progress in bibliography in lines bordering on chemistry. Suggestions as to topics, methods, channels of publication, &c., will be cordially furnished by the Committee. Address correspondence to the Chairman, at Cosmos Club, Washington, D.C.

*Committee :*—

H. CARRINGTON BOLTON, Chairman,
F. W. CLARKE,
A. R. LEEDS,
A. B. PRESCOTT,
ALFRED TUCKERMAN,
H. W. WILEY.

**The Chemical Laboratory of Wiesbaden.**—In the Summer Term, 1896, there were 63 students on the books. Of these, 39 were from Germany, 12 from Russia, 4 from England, 2 from Holland, 2 from North America, 1 from Austro-Hungary, 1 from Switzerland, 1 from Italy, and 1 from Spain. The assistants in the instruction laboratory were three in number, in the private laboratory twenty-one, and in the Versuchsstation two. Besides the director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged, as teachers in the establishment, Prof. Dr. H. Fresenius, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Lenz, Dr. L. Grünhut, and Architect T. Brahm. The next Winter Term begins on the 15th of October. In the different departments of the Laboratory and in the Versuchsstation, besides the scientific researches, a great number of analyses were undertaken on behalf of manufacture, trade, mining, agriculture, and hygiene.

## DETERMINATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK BY THE AMMONIUM ACETATE METHOD.

### By THOMAS S. GLADDING.

THE oldest method of separating alumina and iron phosphates from lime phosphate is, probably, the ammonium acetate method. This has been severely criticised, and just at present seems to be under condemnation. The following investigation has convinced the writer that, when properly carried out, not only does the method give an accurate separation of iron and alumina from lime phosphate, but also gives a neutral phosphate of uniform composition from which the iron oxide and alumina present may be accurately estimated.

In brief, the method used is this:—If a weakly acid solution of phosphates of iron and alumina, together with a large amount of calcium phosphate, be slowly poured into a strong solution of ammonium acetate made acid with acetic acid, the iron and alumina are precipitated as phosphates, upon digestion for a short time at a gentle heat. This precipitate, however, contains more or less calcium phosphate, which is removed by several re-precipitations. I shall demonstrate by experiment :—

*First.* That upon continued re-precipitations of iron and alumina as phosphates in this manner, there is no appreciable diminution of the quantity of either finally obtained, provided there always be a large excess of phosphoric acid present.

A standard solution was made by dissolving 20 grms. of ammonia alum (C. P.) in distilled water. This was slightly acidified with hydrochloric acid, in order to prevent the alumina from separating on standing, and diluted to 1 litre. This solution, upon being standardised, was found to contain the theoretical amount of alumina, that is—

Ten c.c. = $0.0225$ grm. $Al_2O_3$.

One precipitation, in the manner described above, of the alumina in 10 c.c. gave—

| | $Al_2O_3.P_2O_5$, found. | $Al_2O_3$. |
|---|---|---|
| 1 | $0.0545$ | $0.0228$ |
| 2 | $0.0549$ | $0.0229$ |
| 3 | $0.0546$ | $0.0228$ |
| 4 | $0.0540$ | $0.0226$ |
| 5 | $0.0545$ | $0.0228$ |

Three successive precipitations, in which 1 grm. of ammonium phosphate was added before each precip.tation, gave—

| | $Al_2O_3.P_2O_5$. | $Al_2O_3$. |
|---|---|---|
| 1 | $0.0550$ | $0.0230$ |
| 2 | $0.0547$ | $0.0229$ |
| 3 | $0.0544$ | $0.0227$ |

Five successive precipitations were also tried under the same conditions, with the following results :—

| | $Al_2O_3.P_2O_5$ | $Al_2O_3$. |
|---|---|---|
| 1 | $0.0536$ | $0.0224$ |
| 2 | $0.0530$ | $0.0222$ |

When, however, the excess of phosphoric acid was omitted before the re-precipitations, there was a loss of alumina.

An iron solution was made by dissolving C. P. iron wire in hydrochloric acid and oxidising it with nitric acid. When carefully standardised it was found that—

Ten c.c. = $0.0296$ $Fe_2O_3$.

Three successive precipitations, adding 1 grm. ammonium phosphate before each, gave—

| | $Fe_2O_3.P_2O_5$. | $Fe_2O_3$. |
|---|---|---|
| 1 | $0.0545$ | $0.0289$ |
| 2 | $0.0550$ | $0.0291$ |
| 3 | $0.0548$ | $0.0290$ |

Five successive precipitations, in the same way, gave—

| | Fe$_2$O$_3$.P$_2$O$_5$. | Fe$_2$O$_3$ |
|---|---|---|
| 1 | 0·0550 | 0·0291 |
| 2 | 0·0560 | 0·0297 |

*Second.* That upon three successive precipitations in the presence of a large amount of calcium phosphate, as is the case in the analysis of rock phosphate, the precipitate of the phosphates of iron and alumina is sufficiently pure to be taken as such. Of the standard solutions, 5 c.c. of each would together give a precipitate of combined phosphates about equal to that usually found in 1 grm. of phosphate rock. The mixture so analysed was made up as follows :—

Five c.c. alumina solution = 0·01125 Al$_2$O$_3$.
Five c.c. iron solution = 0·01480 Fe$_2$O$_3$.
0·7000 grm. calcium phosphate.

This was given three precipitations, the excess of phosphoric acid being supplied before the second and third precipitations.

| Phosphates obtained. | Al$_2$O$_3$ obtained. | Fe$_2$O$_3$ obtained. |
|---|---|---|
| 1   0·0552 | 0·0115 | 0·0146 |
| 2   0·0540 | 0·0110 | 0·0146 |
| 3   0·0537 | 0·0109 | 0·0146 |
| 4   0·0536 | 0·0109 | 0·0146 |

The iron oxide was determined by volumetric method in the ignited precipitate, and the alumina by subsequent calculation.

In addition, 20 c.c. alumina solution, containing 0·0450 grm. Al$_2$O$_3$, together with 0·700 grm. calcium phosphate, were given three successive precipitations in the same way, with the following results :—

| | Al$_2$O$_3$.P$_2$O$_5$ obtained. Grm. | Al$_2$O$_3$ obtained. Grm. |
|---|---|---|
| 1 | 0·1092 | 0·0456 |
| 2 | 0·1074 | 0·0449 |

In order to prove that the aluminum phosphate precipitated was the normal phosphate, the ignited precipitates were fused, and the phosphoric acid in them estimated.

| | Al$_2$O$_3$.P$_2$O$_5$. | P$_2$O$_5$ obtained. | Al$_2$O$_3$ by diff. | Al$_2$O$_3$ by calc. |
|---|---|---|---|---|
| 1 | 0·0538 | 0·0313 | 0·0225 | 0·0225 |
| 2 | 0·0533 | 0·0312 | 0·0221 | 0·0223 |

The phosphate of alumina is multiplied by the factor 0·418 to obtain the alumina.

Therefore, in determining iron oxide and alumina in phosphate rocks, proceed as follows :—

Four grms. of the finely-ground sample, previously freed by a magnet from any metallic iron derived from the iron mortar used in grinding the sample, are digested for half an hour, at a temperature just below the boiling-point, with about 30 c.c. dilute hydrochloric acid (1—1). This will prevent the solution of any pyrites, if present. Filter and wash thoroughly into a 200 c.c. flask, add a little nitric acid, and boil to oxidise the iron; cool, and fill to mark with water. Take two portions, 50 c.c. = 1 grm., 25 c.c. = ½ grm, and proceed with each as follows :—

Almost neutralise the solutions with strong ammonium hydroxide until the precipitate formed dissolves with difficulty, and thoroughly cool by placing the beaker in a dish of cold water. The neutralisation is then completed by carefully adding dilute ammonium hydroxide until the precipitate remains permanent, then just dissolve by adding dilute hydrochloric acid, drop by drop, stirring well. Have ready in another beaker a mixture of 15 c.c. of a strong solution of ammonium acetate (made by neutralising 30 per cent acetic acid with strong ammonium hydroxide) and 5 c.c. of acetic acid. Carefully pour the cold faintly acid solution of phosphates in a fine stream into this mixture, stirring all the while. Digest at 60° C. from one-half hour to one hour, until the supernatant liquid is clear and the flocculent precipitate is well settled to the bottom.

Filter and wash the precipitate once with a 10 per cent ammonium acetate solution, merely rinsing out the beaker in which the precipitation was made. Dissolve the precipitate from the paper into the same beaker with a few c.c. of hot dilute hydrochloric acid (1—4). Use as little acid as possible, in order to keep the bulk of the solution small. Add 1 grm. of ammonium phosphate, neutralise with ammonium hydroxide, and add hydrochloric acid until the precipitate just dissolves as before, and pour into a mixture of 15 c.c. ammonium acetate solution and 5 c.c. acetic acid. Digest at 60° C. for one-half to one hour and filter, and wash once with the 10 per cent ammonium acetate solution. Re-dissolve and repeat the precipitation, being careful to again add 1 grm. of ammonium phosphate to the solution, in order that there be a sufficient excess of phosphorus pentoxide to precipitate all the alumina as a neutral phosphate. Wash the precipitate three times with dilute ammonium acetate solution.

Take the filter, while wet, from the funnel, and ignite in a tared platinum capsule, using a very low flame until the filter-paper is thoroughly charred. The heat is increased gradually until the paper is completely consumed, and finally the blast-lamp is used for a minute. Weigh as combined phosphates of iron and alumina. The iron is determined volumetrically in the solution of the weighed precipitates. The iron oxide present in the rock is also determined separately by volumetric process, preferably the bichromate method, in a solution of 5 grms. of the rock in dilute hydrochloric acid (1—1), reducing all iron to protoxide and titrating with bichromate.

The ignited precipitate from one of the duplicate precipitations may, if desired, be dissolved and subjected to a fourth precipitation, and the filtrate tested for lime by adding ammonium oxalate and heating. My thanks are due to our assistant, Thomas Brown, jun., for valuable aid in the above analytical determinations.—*Journal of the American Chemical Society*, vol. xviii., No. 8.

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## ON SOME NEW SOUTH WALES AND OTHER MINERALS.[*]

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

*Antimonite.*—Queensland.

A HARD splintery variety, breaking with a conchoidal fracture with somewhat hackly surfaces; noticeable as containing silica and barytes in thin veins or joints.

*Analysis.*

| | |
|---|---|
| Antimony .. .. .. .. .. | 64·47 |
| Sulphur.. .. .. .. .. .. | 26·59 |
| Iron .. .. .. .. .. .. | 1·00 |
| Silica .. .. .. .. .. .. | 3·41 |
| Barium sulphate.. .. .. .. | 2·63 |
| Undetermined and loss .. .. | 1·90 |
| | 100·00 |

The above is the mean of two analyses. Sp. gr. 4·43.

*Apatite, Plumbiferous.*—Calcium fluo-phosphate.
Broken Hill.

Some specimens of apatite containing lead were forwarded to me by Mr. S. Harris, from Block 14 Mine for examination.

The apatite is in the form of small grey imperfect crystals (some, however, are symmetrical hexagonal prisms closed by the pyramid and terminal pinacoids), about one-sixteenth inch long, in cavities in a matrix of dark blue-black honey-combed crystalline zinciferous galena; the freshly fractured apatite has somewhat the lustre and

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[*] Read before the Royal Society of N. S. Wales.

appearance of pyromorphite. It is probable that part of the calcium phosphate of the apatite is replaced by the isomorphous lead phosphate.

The crystals of apatite were separated as carefully as possible from the galena, but this could not be done completely, as small crystals of galena are seen within the apatite crystals, *i.e.*, when sliced and examined under the microscope.

Mr. Harris states that pyromorphite was met with in the shallower parts of the same portion of the mine in considerable quantities. He found 3·9 per cent of fluorine, 0·5 per cent manganese monoxide, and 36·25 per cent of phosphorus pentoxide, but as all the specimens I examined showed enclosed lead sulphide, I do not quote his amounts of lead and lime; the proportions of phosphoric oxide and fluorine indicate that the mineral answers to the general formula of $3Ca_3P_2O_8,CaF_2$, in which part of the Ca is probably replaced by Pb.

### *Barklyite.*—Two Mile Flat, Mudgee, N.S.W.

Collected by the late Prof. A. M. Thomson, Sydney University.

The specimens were in small well-rolled pebbles, not more than ¼ inch long. Most are of a kind of dull magenta colour and usually show one or two light streaks or veins; in others, the colour might be referred to that of lean beef. Hardness about 8·5, *i.e.*, less than 9. Sp. gr. 3·738 at 18·5° C.

The mineral is tough, and the fracture granular and of a pink tint; the powder is also of a pale pink tint. Before the blowpipe it darkens a little and returns to its former colour on cooling. After ignition it is a little more opaque, probably due to slight disintegration. When strongly heated it becomes brilliantly luminous and gives a blue colour with cobalt nitrate. Large quantities give the chromium reaction with microcosmic salt and borax beads. The precipitate of $Al_2O_33H_2O$, fused with $NaKCO_3$ gave the manganese reaction in one case but not in others.

No full description of this mineral appears to have been published; the name barklyite was given to it by Mr. Geo. Milner Stephen, F.G.S., after the then Governor of Victoria. In a catalogue of his collection, and in a lecture, he refers to them as violet rubies, or barklyite, from the Ovens district in Victoria (*Trans. Roy. Soc. Vict.*, 1865, p. 70). Apparently, too, it has never been met with in any quantity, and the variety does not appear to be sufficiently distinct to warrant a special name.

It consists principally of alumina ($Al_2O_3$), but the analysis in hand is not yet completed.

### *Chrysocolla.*—Hydrous Copper Silicate. Broken Hill, N.S.W.

As incrustations and stalactitic forms, with mammillated surfaces, of a sky blue and green colour. Vitreous lustre in parts; conchoidal fracture; hardness, 4; streak, pale blue. Effervesces slightly on warming with HCl, from the presence of a little copper carbonate. Before the blowpipe it darkens and breaks up slowly with decrepitation. In tube it gives off much water and a nitrogenous odour. Soluble in HCl and $HNO_3$ with a residue of silica.

### *Beryl.*—Vegetable Creek, New England, N.S.W.

Described in a paper read before the Royal Society of New South Wales, December 2, 1891. Sp. gr. 2·80; hardness, 7·5.

#### *Analysis.*

| | |
|---|---|
| Silica .. .. .. .. .. .. | 67·4 |
| Alumina .. .. .. .. .. | 18·5 |
| Beryllia.. .. .. .. .. .. | 12·9 |
| Iron sesquioxide .. .. .. .. | 0·6 |
| Lime .. .. .. .. .. .. | traces |
| | 99·4 |

### *Crocoisite.*—Dundas, Tasmania.

In brilliant crystals of a deep orange-red colour, about ½ inch long, seated on a mangano-ferruginous matrix. The Dundas mines have yielded some fine groups of crocoisite crystals, with the prisms several inches long; associated with cerussite, galena, and occasionally anglesite and other lead minerals. Hardness, 2·5; sp. gr. 5·92.

#### *Analysis.*

| | |
|---|---|
| Lead monoxide .. .. .. .. | 66·86 |
| Chromium trioxide .. .. .. | 30·99 |
| Iron sesquioxide .. .. .. .. | 1·02 |
| | 98·87 |

Which corresponds with the formula $PbCrO_4$.

### *Fahlerz.*—Wiseman's Creek, *via* Brewongle, N.S.W.

Occurs in quartz veins. Collected in September, 1888. No crystals were obtained.

#### *Analysis.*

| | |
|---|---|
| Copper .. .. .. .. .. | 33·004 |
| Lead .. .. .. .. .. .. | 0·630 |
| Iron .. .. .. .. .. .. | 2·844 |
| Zinc .. .. .. .. .. .. | 3·693 |
| Antimony .. .. .. .. .. | 34·620 |
| Sulphur .. .. .. .. .. | 25·207 |
| Nickel .. .. .. .. .. .. | trace |
| Cobalt .. .. .. .. .. .. | trace |
| | 99·998 |

The above corresponds approximately to—

$$\tfrac{4}{5}CuS,\tfrac{1}{5}(FeZn)S,Sb_2S_3.$$
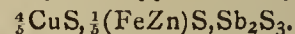
Some silica was obtained in the analysis, but this was deducted and an allowance made for it in the calculation, as it obviously belonged to the matrix.

A special examination was made for gold and silver on a larger quantity, when 31 ozs. 17 dwts. 0 grs. of silver, and 2 ozs. 13 dwts. 8 grs. of gold per ton were found.

### *Ilmenite.*—Cloncurry River, Queensland.

Black, with traces of crystal planes, breaks with well-marked metallic lustre.

#### *Analysis.*

| | | | |
|---|---|---|---|
| Titanium dioxide, $TiO_2$ | .. | .. | 49·85 |
| Silicon     ,,    $SiO_2$ | .. | .. | 1·01 |
| Iron monoxide, FeO | .. | .. | 35·70 |
| Iron sesquioxide, $Fe_2O_3$ | .. | .. | 13·22 |
| | | | 99·78 |

Manganese and magnesium are usually met with, but they and other metals, although specially sought for, were not found in this specimen. Dana gives the following extremes:—

| | | |
|---|---|---|
| $TiO_2$ .. .. | = 59·20 to 3·55 per cent |
| FeO .. .. | = 46·53 to 3·26  ,, |
| $Fe_2O_3$.. .. | = 93·63 to 1·20  ,, |

### *Zinciferous Galena.*

This mineral was sent to me from Broken Hill as clausthalite, the selenide of lead. Before the blowpipe it yielded the reactions lead, zinc, and sulphur, with a little arsenic, but I could not get any reaction for selenium. Decrepitates strongly. It appears to occur in nodular masses.

The mineral in certain lights has a dull grey colour and scoriaceous appearance, but in other positions the light is reflected from it brilliantly with a bluish grey metallic lustre; this is due to the fact that the surface is covered with minute cubical crystals, which have their planes more or less parallel, although at different levels; my specimens only exposed about 2 square inches, but I think it would be found to extend over larger surfaces. The effect is something like that of " shot " silk.

Under a 1 inch objective the cubical character of the crystals are clearly recognisable, so also are the well-marked cubical cleavage planes, which have a strong metallic lustre. The mineral appears to be homogeneous, and no separate portions of blende were detected in it, so that the two sulphides seem to have been deposited together; thin films of arborescent copper pyrites occur on some of the surfaces, and within crevices. Sp. gr. at 18° 6·72. It is slightly harder than galena.

The nodules only contain a little zinc; but they have not yet been analysed; on assay they proved to be very rich in gold, and gave me 5 ozs. 17 dwts. 4 grs. per ton, and 0 oz. 19 dwts. 4 grs. of silver per ton; lead minerals are usually richer in silver than in gold.

The vein stuff gave—

*Analysis.*

|  | I. | II. | III. |
|---|---|---|---|
| Insoluble | 3·16 | 3·47 | — |
| Lead | 60·20 | — | 61·014 |
| Zinc | 15·50 | 14·85 | — |
| Sulphur | 18·94 | — | — |
| Iron | 2·62 | — | — |
| Copper | 0·205 | — | — |
| Arsenic | traces | — | — |
| Antimony | traces | — | — |
|  | 100·625 | | |

The proportion is about $3PbS, 2\frac{1}{2}ZnS$.

It seems to be related to the minerals huascolite and kilmacooite (Dana's "System of Mineralogy," 1892, p. 51), but with fairly well marked differences. I do not, however, think it need be named; the term zinciferous galena describes it accurately without adding to the already excessive list of so-called new species of minerals.

*Limestone with Cone-in-cone Structure.*—Picton, N.S.W.

Evidently very impure, of a brown colour, and argillaceous appearance. An analysis of this was made in 1876, and forwarded to the Mineralogical Society, but lost in transit.

*Composition.*

Portion soluble in HCl :—

| | |
|---|---|
| Water | 2·10 |
| Carbon dioxide, $CO_2$ | 30·01 |
| Silica, $SiO_2$ | 1·63 |
| Iron sesquioxide, $Fe_2O_3$ | 4·35 |
| Manganese oxide, $MnO$ | 0·52 |
| Lime, $CaO$ | 38·19 |
| Soda, $Na_2O$ | 1·70 |
| Portion insoluble in HCl | 22·21 |
| | 100·71 |

The amount of calcium carbonate being 68·20. The portion insoluble in hydrochloric acid was not further examined.

The specimen was from a layer about three inches thick; the cones are fairly regular in size and shape, and run right through the deposit in vertical columns, like piles of small closely packed conical paper sugar-bags; the average diameter being about half an inch, and the length perhaps a little more, the angle of the cone being between fifty and sixty degrees, and incipient crystallisation is visible in parts. The upper surface of the deposit presents pits with thickened edges over some of the columns of cones.

Mr. A. J. Sach, F.C.S., published an account of this deposit (with an analysis) in the "Report of the Australasian Association for the Advancement of Science," Hobart Session, 1892, p. 328.

*Molybdenite.*

This was described in "Note No. 6," read before this Society, December 2, 1891, as occurring in large crystals, $3 \times 3\frac{1}{2} \times 5\frac{1}{2}$ inches long, from the Eleanora Mine, Kingsgate, near Glen Innes, N.S.W.

*Composition.*

|  | I. | II. |
|---|---|---|
| Molybdenum | 57·31 | 58·66 |
| Sulphur | 42·00 | 41·23 |
| Iron | 1·50 | 0·39 |
|  | 100·81 | 100·28 |

Another specimen yielded about 6 per cent of manganese oxide; but this was probably mechanically enclosed between the plates of molybdenite. Sp. gr. 4·6.

*Proustite.*—Silver Sulpharsenide.

Mr. Edgar Hall, F.C.S., sent me, in August last, some specimens from his United Mine at Rivertree, in which he had found some minute red crystals. I have examined the crystals, and agree with him in regarding them as proustite. They are quite microscopic, and it is difficult to examine them and still more to separate them from the matrix.

Mr. Hall states that they occur in a narrow vein, about half an inch thick on the hanging wall, and that they have been met with at 70 feet, 120 feet, and 180 feet levels; in fact, all the way down so far. The lode is a contact one, between a dyke of quartz diorite and the massive granite of the country. The fissure is about 8 feet wide at the 120-feet level, of which about 4 feet is quartz carrying argentiferous minerals; the yield of silver is found to be much greater where the proustite crystals are present.

The crystals are on a bluish quartz, containing mispickel; they are of a full red colour, translucent, with vitreous lustre, and about one-tenth to one-fifth m.m. in length. I was able to obtain the reactions for arsenic, sulphur, and silver, but no attempt was made to make a quantitative analysis, as it was only with difficulty that a few hundredths of a grain were obtainable.

Proustite is reported by Mr. C. Marsh ("Geology of the Broken Hill Lode, &c.," by J. B. Jaquet, p. 90, Sydney, 1894) to occur also at Broken Hill.

*Scheelite.*—Calcium Tungstate, $CaWO_4$.

Lady Hopetoun Mine, Glen Innes, N.S.W.

Massive, coarsely crystalline, of a pale brownish stone colour. Hardness, 5; sp. gr. 5·93, another portion 5·3 only.

A fairly pure calcium tungstate, containing a little water, 2·23 per cent of silica, 1·52 per cent of iron sesquioxide, and a trace of manganese.

*Tinstone Crystals.*—Elsmore Mine, Inverell, N.S.W.

In stout pyramids, usually about half an inch through, but some of them are much larger. Very slightly water-worn at the edge, otherwise the crystals have the faces of the pyramid well developed and of a high metallic lustre. Yielded a white powder. Sp. gr. 6·68; hardness. 6·5.

*Analysis.*

| | |
|---|---|
| Tin oxide, $SnO_2$ | 94·60 |
| Silica, $SiO_2$ | 2·00 |
| Iron sesquioxide, $Fe_2O_3$ | 1·67 |
| Manganese oxide, $MnO$ | 0·25 |
| Tungstic acid, $WO_3$ | 0·06 |
| | 98·58 |

Another specimen from the same locality, but water-worn, was found to be harder, = 7, with a sp. gr. of 6·54. The powder of this was brown.

*Analysis.*

| | |
|---|---|
| Tin oxide, $SnO_2$ | 92·52 |
| Silica, $SiO_2$ | 1·68 |
| Oxide of manganese, $MnO$ | 0·98 |
| Iron sesquioxide, $Fe_2O_3$ | 3·21 |
| Tungstic acid, $WO_3$ | 0·36 |
| | 98·75 |

The loss of 1·25 on this and 1·42 on the previous specimen may indicate the presence of some of the rarer elements not specially sought for, and that the specimens are worthy of further examination.

### Topaz.—Shoalhaven District.

In the form of short columnar prisms, the terminal pyramidal planes not well developed, seated on granite. Of a greyish tint, more or less opaque, but translucent in parts.

Most of the crystals were about one-fifth to one-fourth inch in diameter, and about ½ inch long, closely packed together so as to form a solid layer of topaz next to the supporting rock. The crystals are brittle, some of the faces are slightly rough, as if etched. Hardness, 7·5 only; sp. gr., 3·56.

Before the blowpipe it decrepitates, darkens, but becomes nearly colourless again on cooling. Gives off a little water when heated in tube.

### Analysis.

| | |
|---|---|
| Silica .. .. .. .. .. .. | 28·19 |
| Alumina .. .. .. .. .. | 62·66 |
| Fluorine .. .. .. .. .. | 14·01 |
| Water at 100° .. .. .. .. | 1·21 |
| | 106·07 |

The above are the mean of the results of two closely agreeing analyses. The oxygen equivalent to the fluorine must be allowed for in the above analysis.

In the foregoing paper I was assisted by Mr. A. O. Black, a student in the Chemical Laboratory, who, under my direction, made several of the analyses; Mr. C. Walker, another student, analysed the ilmenite; Mr. J. A. Schofield, A.R.S.M., F.C.S., Demonstrator, the zinciferous galena; and Mr. J. M. Petrie, Junior Demonstrator, the fahlerz.

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## THE SEPARATION OF TRIMETHYLAMINE FROM AMMONIA.*

### By HERMANN FLECK.

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THE quantitative estimation of trimethylamine in presence of ammonia is, I believe, not mentioned in the literature, although a number of publications have appeared in which the detection of trimethylamine, in presence of ammonia, by means of the different solubilities of their hydrochlorides in absolute alcohol, has been successfully carried out.

Dessaignes (*Ann. Chem.*, Liebig, lxxxi., 106) prepared and analysed with good results the platinum double salt of trimethylamine, by conducting the mixture of ammonia and trimethylamine vapours into hydrochloric acid, evaporating to dryness, extracting with absolute alcohol, precipitating with platinic chloride, and re-crystallising the precipitate formed several times from hot water.

Wicke (*Ann. Chem.*, Liebig, xci., 121) adopts the same method, using, however, alcohol-ether extract.

Winkeles (*Ann. Chem*, Liebig, xciii., 321), in using this method, further states that while ammonium chloride is soluble to some extent in absolute alcohol, it is rendered totally insoluble by the presence of salts of such bases as trimethylamine.

Eisenberg (*Ber. d. Chem. Ges.*, 1880, 1669), by a similar procedure, obtained the platinum double salt in crystals of great purity and perfection.

The success in each case is undoubtedly due to the fact that large quantities of hydrochlorides were used. Winkeles (*loc. cit.*), for example, employed the hydrochlorides obtained from 26 gallons of herring brine. Further the mixtures were very rich in trimethylamine.

This method applied to a substance containing a low percentage of the latter yielded results which clearly show that trimethylamine hydrochloride does not render ammonium chloride insoluble in absolute alcohol, and further does not serve as a good means of qualitative, much less of quantitative, separation. A portion of the mixture containing trimethylamine and ammonia was saturated with hydrochloric acid, evaporated to dryness, and extracted several times with portions of several times the volume of boiling absolute alcohol. The alcoholic extract evaporated to dryness gave 18 per cent of supposed trimethylamine hydrochloride. To identify the latter, the residue was taken up with alcohol and platinic chloride added. The precipitate formed was re-dissolved in boiling water, and the different fractional crystallisations, consisting of octahedra, analysed.

| | Pt found. | Required for |
|---|---|---|
| First crystallisation | 43·6 | $(NH_4Cl)_2PtCl_4$, 43·84 |
| Last „ | 39·5 | Corresponding to a mixture of |

$$2 [(NH_4Cl)_2PtCl_4] +$$
$$3 [N(CH_3)_3 \cdot HCl]_2 PtCl_4,$$

which require 39·4 p.c. Pt.

Intermediate crystallisations gave intermediate, gradually decreasing results, showing that the isomorphous forms of the two salts crystallised together.

Duvillier, Buisine (*Ann. Chem.*, Liebig (5), xxiii., 299) extract the mixed *sulphates* to prepare pure trimethylamine from the technical product. The suggestion led to the use of the following method, which yielded satisfactory results.

The mixed hydrochlorides are repeatedly extracted with portions of five or six times the volume of boiling absolute alcohol, and the solvent distilled off in a three-quarter litre distilling bulb. An excess of caustic soda is added to the residue, and the gases formed on boiling driven over into a large quantity of water. Litmus is added, followed by the exact quantity of dilute sulphuric acid required to neutralise. The liquid is evaporated to dryness and extracted with 1 litre cold absolute alcohol in which trimethylamine sulphate dissolves, leaving ammonium sulphate undissolved. The alcohol is distilled off, the residue transferred to a weighed dish, dried, and weighed. In this manner 32·910 grms. of the carefully-dried mixed chlorides gave 2$\frac{5}{10}$ grms. trimethylamine sulphate, corresponding to 2·21 grms. hydrochloride, or 6·71 per cent.

That the extraction was complete is evident from the total absence of the fishy odour when the extracted residues are treated with alkali. That the extracted material is pure is shown by the following analyses of the octahedral crystals of the platinum double salt prepared from the trimethylamine sulphate:—

| | | | Required for $[N(CH_3)_3 \cdot HCl]_2 \cdot PtCl_4$. |
|---|---|---|---|
| | | Per cent Pt. | Per cent Pt. |
| I. | 0·0983 grm. gave .. | 36·92 | — |
| II. | 0·3017 „ .. | 37·12 | 36·93 |

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## VOLUMETRIC ESTIMATION OF HYDROXIDES AND CARBONATES; AS ALSO OF THE MONO- AND BICARBONATES OF THE ALKALIS, ALKALINE EARTHS, AND MAGNESIA.

### By C. KIPPENBERGER.

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THE author has used a series of colouring-matters as indicators. In general they may be used along with methyl-orange, which is not sensitive to carbonic acid, thus frequently simplifying the operation. The change of colour of these indicators is shown in the accompanying table.

| By— | Hematoxyline. | Gallein. | Alkanin. | Gentiana blue. | Blue de Lyon. | Poirrier's Blue. |
|---|---|---|---|---|---|---|
| Hydroxide .. .. .. .. | Blue | Blue | Blue | Deep blue | Red | Red |
| Alkali { Carbon. | Red | Blue, turning red | Blue | Red | Red | In strong solutions red, turning blue. |
| Alkali { Bicarb. | | Red | Red | Blue | Blue | Blue |
| Alk. earths { Carbon. | Red | Red | Red | Blue | Blue | Blue |
| Alk. earths { Bicarb. | | | | | | |
| Magnesium { Carbon. | | Blue | Blue | } Blue { | Red | } Blue |
| Magnesium { Bicarb. | | Red | Red | | Blue | |

Hematoxyline was tried with magnesium carbonate and mixtures of alkaline hydroxide and carbonate. In the former case the results were too low by $\frac{1}{8}$; in the second there is formed, on the addition of the indicator, a dark mixed colour which after the hydroxide has been converted into a salt changes to the red colouration characteristic of the alkaline carbonate.

Gallein certainly colours a mixture of alkaline hydroxide and carbonate blue; but on the addition of an acid the red colouration does not appear when the hydroxide is converted into a neutral salt and the carbonate into bicarbonate, but earlier. The author refers this phenomenon to the formation of sesqui-carbonate, which effects the change. When gallein is used the acid must not be too strong, centinormal sulphuric acid being the most suitable. Stronger acid occasions a development of carbonic acid, which has a disturbing effect. The results, however, do not agree very well even on the use of this dilute acid.

Phenolphthalein, alkanin, and blue de Lyon are not sensitive to sesquicarbonates, and are therefore more suitable than hematoxyline and gallein for the abovementioned substances when jointly present. Gentiana blue cannot well be used along with decinormal and centinormal liquids.

Poirrier's blue ($C_4B$) yields, according to Engel and Ville, a blue colour with alkaline carbonates and a red with hydroxides. Kippenberger observed that in concentrated solutions carbonates also give a red colour, and the blue colouration makes its appearance when the solution has the strength of a normal liquid. Sesquicarbonates and bicarbonates show a rather lighter blue colour. Water is not without influence on the colour, and liquids which are more dilute than decinormal cannot be titrated. The author observed, as had been previously done by Lunge, that the results obtained with Poirrier's blue are always too low.

Sulphindigotic acid, which has been also recommended by Engel and Ville, gives no accurate results.

Flavescin, recommended by Lux (Zeit. Anal. Chemie, xix., 459) gives very useful results. The author, however, does not use this indicator alone, but along with methylorange, like the foregoing. This procedure has the advantage that, after the conversion of the hydroxide into neutral salts, and of the carbonate into bicarbonate, it is possible to titrate to the conclusion in the cold, whilst, according to Lux, the liquid is boiled after the addition of more acid, and after the expulsion of the carbonic acid it is titrated back with lye until yellowness.

The calculation, on employment of the titration-method, is simple. At first the hydroxide and the half of the carbonate is neutralised, and then the second half of the carbonate is titrated, using methyl-orange as an indicator. If mono- and bicarbonate are jointly present, the half of the former is determined in the first phase, and then the other half of the former and the bicarbonate are determined in the second phase.

Dissolved hydroxides of the alkaline earths along with alkaline hydroxides can be determined by first effecting a general determination, and then, in another portion of the liquid, after precipitation of the hydroxides of the alkaline earths with a standard solution of carbonate, the hydroxide and carbonate are then determined in an aliquot portion, as above described. Magnesium carbonate in presence of alkali carbonate, is determined in an analogous manner, when we add (whilst heating) alkaline hydroxide and titrate magnesium carbonate with the use of hematoxyline, where, however, only two-thirds of the whole are determined.—Zeitschrift für Analyt. Chemie, xxxv., Part 3, p. 334.

## ON A DISTINCTIVE CHARACTER OF ORDINARY MAGENTA AND OF ACID MAGENTA S.
## ON SCHIFF'S REACTION.

By P. CAZENEUVE.

MAGENTA or rosaniline hydrochlorate, and more generally all the salts of this base, possess the property, if decolourised with sulphurous acid, of giving—in contact with alcohol mixed with ordinary aldehyd or its kindred homologues—a violet colouration differing from the shade of the original magenta. The aromatic aldehyds, likewise, give the re-colouration.

A very small quantity of aldehyd sets up the reaction (Schiff). We may proceed in the following manner :—

Some c.c. of an aqueous solution of a salt of rosaniline, at $\frac{1}{1000}$, are decolourised with a solution of sulphurous acid. The addition of alcohol, mixed with formic or with ethylic aldehyd, likewise developes the violet colouration.

Magenta S, a commercial acid magenta, which is in reality a sodium rosaniline di- or trisulpho-conjugated, if similarly treated gives nothing,—that is, the solution, if decolourised with sulphurous acid, does not turn to a violet on the addition of alcohol charged with aldehyd.

According to the proportion of alcohol added the decolourised solution resumes a rose tint, which is the original colour much diluted. It must otherwise be noted that the richer the alcohol in aldehyd the less does this light rose tint appear.

The addition of hydrochloric acid does not modify the negative result obtained with magenta, but it accentuates the colouration given by the salts of ordinary rosaniline.

These two magentas, therefore, behave in a very different manner with alcohol charged with aldehyds. This fact merits the more notice as some authors assert that ordinary magenta and magenta S behave in an identical manner with reagents.

This assertion is already erroneous, because we know that magenta S, if heated with an alkali, does not enter into amylic alcohol like ordinary magenta, and that it resists the oxidising action of manganese peroxide, as I have already shown for its detection in wines.

To return to the action of aldehyds :—If we wish to proceed methodically, and prepare the conditions for this differential reaction in a course of lectures on colouring-matters, we may prepare the following solutions, the one made with an ordinary salt of rosaniline and the other with magenta S.

| | |
|---|---|
| Water .. .. .. .. .. .. .. | 200 c.c. |
| Solution of magenta at $\frac{1}{1000}$ .. .. | 30 ,, |
| Sodium bisulphite at sp. gr. 1·288 .. | 20 ,, |
| Sulphuric acid at sp. gr. 1·767 .. .. | 3 ,, |

The addition of 4 c.c. of alcohol at 50 p. c. containing formic or ethylic aldehyd serves to distinguish the two solutions to the eyes of the pupils.

In a recent note on Schiff's reaction, M. Urbain sees, in this re-colouration of aldehyds of magenta which had been decolourised by sulphurous acid, the sign of the formation of condensation-products of the aldehyds and rosaniline, compounds which sulphurous acid does not decolourise.

This is only an hypothesis which requires to be proved by the isolation and the analysis of the colour formed.

In all cases, if this hypothesis is confirmed, the inaptitude of sulpho-conjugated rosaniline to become coloured in presence of the aldehyds leads us to think that the fixation of the aldehyds on the rosaniline molecule takes place at the same point of the nucleus where the sulpho-conjugation is effected.—*Bulletin de la Soc. Chimique de Paris*, Series 3, vol. xv.—xvi., p. 723.

## THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER von JONSTORFF (Neuberg, Austria).

(Continued from p. 102).

4. *Errors in the Operations..*—These include the unavoidable losses in the analysis, the action which results from the glass and porcelain vessels being attacked, the variations in the ash contents of the filters used, &c. In this connection some of the numerous researches relating to these points may be referred to. According to R. Cowper (*Journal of the Chemical Society*, 1882, p. 254), when the following solutions, in quantities of 100 c.c., are heated for six days in glass vessels to 100° C., the following amounts of glass are dissolved:—

| Reagent. | Glass dissolved in 100 c.c. Grm. | |
|---|---|---|
| Water .. .. .. .. .. .. | 0·0080 | 0·0100 |
| Sulphuretted hydrogen water .. | 0·0125 | 0·0087 |
| Dilute ammonium sulphide (prepared from 0·982 sp. gr. ammonia) .. .. .. .. .. | 0·0496 | 0·0525 | 0·0512 |
| Concentrated ammonium sulphide (prepared from 0·88 sp. gr. ammonia) .. .. .. .. | 0·0340 | 0·0472 |
| Ammonia of 0·982 sp. gr. .. | 0·0258 | 0·0425 |
| Conc. ammonia, 0·88 sp. gr. .. | 0·0075 | 0·0077 |

* Read before the Iron and Steel Institute.

R. Weber and Sauer (*Zeit. f. Ang. Chemie*, 1891, p. 662; *Ber. Deut. Chem. Ges.*, vol. xxv., pp. 70 and 1814) boiled various solvents in 100 c.c. flasks, made of different kinds of glass, replacing constantly the liquid boiled away, and obtained the results shown in the accompanying table.

Porcelain vessels are, as a rule, much less attacked. Thus R. Fresenius found that when the solvents named were boiled in Berlin porcelain dishes, the quantities dissolved, expressed in per cent of the solvents, were as follows :—

| Solvent. | Quantity dissolved. | |
|---|---|---|
| Water .. .. .. .. .. .. .. | 0·0005 | |
| Pure hydrochloric acid .. .. .. | 0·0053 | 0·0047 |
| Ammonium chloride solution of 10 per cent strength .. .. .. .. | 0·0393 | |
| Crystallised sodium carbonate solution of 10 per cent strength.. .. | 0·0243 | |

Unfortunately other firms place upon the market porcelain dishes which are very considerably attacked even by concentrated hydrochloric acid.

5. *Errors in the analytical methods* belong to the most important causes of differences in analytical results. They are so numerous and various that it must suffice to mention a few examples.

To these belong the incomplete oxidation of carbon in its determination with the aid of chromic acid and sulphuric acid ; leaving out of consideration the various forms of the carbon in the Eggertz colorimetric method for the determination of carbon ; the sulphur losses, which in all methods for the determination of sulphur that depend on the evolution of sulphuretted hydrogen, result from a portion of the sulphur remaining in the insoluble residue : the error in the manganese assay with lead peroxide due to the ready decomposability of $HMnO_4$, and many others.

I would like just to point out in this connection that these errors may be of a positive as well as of a negative character, that consequently a method where, under certain circumstances, two or more simultaneously occurring inaccuracies exactly counterbalance each other may give very satisfactory results, while in other cases it may leave much, very much perhaps, to be desired, a circumstance which must be taken into consideration in the testing of analytical methods.

Thus, to select a widely-known instance, barium sulphate is not altogether insoluble in ferric chloride, and results would be obtained which would be too low if, in the determination of sulphur, after its complete oxidation to sulphuric acid, it were precipitated with barium chloride in the solution containing ferric chloride. On the other hand, the precipitate obtained in this case is not pure, as it always contains included iron salts in smaller or larger quantity, and this again leads to too

*Percentage Composition of the various Glasses.*

| Variety of Glass. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|---|---|
| Silica .. .. .. | 76·22 | 74·09 | 76·39 | 68·56 | 74·48 | 74·69 | 66·75 | 74·12 | 77·07 | 74·40 |
| Alumina.. .. .. | — | 0·40 | 0·50 | 1·85 | 0·50 | 0·45 | 1·31 | 0·50 | 0·30 | 0·70 |
| Lime .. .. .. | 4·27 | 5·85 | 5·50 | 7·60 | 7·15 | 7·85 | 13·37 | 8·55 | 8·10 | 8·85 |
| Potash .. .. .. | — | 7·32 | 4·94 | 2·24 | 6·64 | 8·64 | 15·50 | 4·86 | 3·75 | 4·40 |
| Soda .. .. .. | 19·51 | 12·34 | 12·67 | 19·75 | 11·23 | 8·37 | 3·07 | 11·97 | 10·78 | 11·65 |
| Totals.. .. | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |
| Silica : lime : alkali | 17:1:4 | 11:1:2·6 | 12·7:1:2 | 10:1:3 | 9·5:1:2 | 8·8:1:1·6 | 4·5:1:0·8 | 8:1:1·6 | 8·8:1:1·5 | 8:1:1·5 |

*Loss of Weight in Milligrammes of a 100 c.c. Flask by the action of—*

| Variety of Glass. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | X. |
|---|---|---|---|---|---|---|---|---|---|---|
| Water, 5 hours .. | 62·5 | 31·5 | 29·5 | 17 | 13 | 9·5 | 7·5 | 7·5 | 5 | 4·5 |
| $H_2SO_4$, 25%, 3 hrs. | ? | 43·5 | 35 | 8 | 7 | 6·5 | 5·5 | 5 | 5 | 3 |
| HCl, 12%, 3 hours.. | 85 | ? | 21 | 4 | 2·5 | 1·5 | 1 | 1 | 0 | ·0 |
| $NH_3$, 10%, 3 hours | ? | ? | 62 | 11 | 8·5 | 7·5 | 7·5 | 6 | 5 | 5 |
| Sodium phosphate, 2%, 3 hours .. | ? | ? | 81 | 64 | 40 | 35·5 | 34 | 30 | 15 | 12·5 |
| Sodium carbonate, 2%, 3 hours .. | 283 | 160 | 130 | 124 | 50·5 | 45 | 42 | 42 | 26·5 | 25 |

high results. In certain circumstances both these sources of error may more or less exactly counterbalance each other, while in others one or the other may get the upper hand, and the result consequently be either too high or too low, as the case may be. Indeed A. Tamm (*Jern-kontorets Annaler*, 1887, p. 4) has based on this circumstance a rapid method for the determination of sulphur.

These occurrences—and they are not always so simple as in the above example—necessitate the most complete investigation, if with certainty either all errors are to be avoided or the most complete possible balance of errors effected, which in many cases leads to exceedingly useful methods.

6. *Personal Errors.*—The errors, too, which are due to this cause are of great importance, especially where the analyses are not effected by trained chemists, but their intimate study is beset with great difficulties. To effect this, a series of parallel analyses should be made by different chemists, using the same method, and with exact and detailed specifications as to the method of working, and as a result in all probability " personal equations " would be obtained, such as have long been known to astronomers.

These personal errors, which have their origin partly in the particular skill of the one or the other in different methods and operations, partly in personal estimations, as in the colorimetric methods, or in other causes, are, however, of particular interest, because it is just these which lead one chemist to prefer one method and another a different one, and not infrequently cause opinions as to one and the same method to be very different.

To these personal errors various occurrences may be referred, as, for instance, the following, mentioned by C. B. Dudley (*Journal of Analytical and Applied Chemistry*, 1893, p. 5):—In a sample of steel Drown found 0·14 per cent of silicon, while on the other hand another chemist found 0·28. A further investigation showed that the first-named chemist had allowed the dish to stand for two days after evaporation and taking up again with water, and had only then filtered off the silica. It was found that the silica had slowly passed into solution again. After two days of 0·28 per cent of silica only 0·14 was present, and after six days only 0·06, a behaviour which would not have been anticipated.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, June 18th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 108).

97. "*The Action of Ethylic β-Iodopropionate on the Sodium Derivative of Ethylic Isopropylmalonate.*" By J. Z. HEINKE and W. H. PERKIN, jun., F.R.S.

These experiments were instituted with the object of obtaining additional evidence as to the constitution of the isopropyl glutaric acid described in the preceding abstract. When ethylic β-iodopropionate is digested in alcoholic solution with the sodium derivative of ethylic isopropylmalonate, the reaction proceeds as follows:—

$$C_3H_7CNa \parallel (COOEt)_2 + I \cdot CH_2 \cdot CH_2 \cdot COOEt =$$

$$= \frac{C_3H_7 \cdot C \cdot CH_2 \cdot CH_2 \cdot COOEt}{\parallel (COOEt)_2} + NaI,$$

and the product formed was found to be identical with the ethylic isopropylpropanetricarboxylate described in the preceding abstract. The ethereal salt on hydrolysis

yielded isopropylpropanetricarboxylic acid (m. p. 165°), and this at 180° yielded isopropylglutaric acid (m. p. 94—95°). A number of derivatives of this acid were prepared, and in this way its identity with the isopropylglutaric acid described in the preceding abstract was conclusively proved.

98. "*The Condensation of Halogen Derivatives of Fatty Ethereal Salts with Ketones and Ketonic Acids.*" By W. H. PERKIN, jun., F.R.S., and J. F. THORPE.

The condensation of substance containing the group > CO with halogen derivatives in the presence of zinc appears to have been first studied by Frankland and Duppa (*Annalen*, cxxxiii., 80); these chemists synthesised ethylic hydroxyisobutyrate,—

$$(CH_3)_2C(OH).COOC_2H_5,$$

by acting on a mixture of methylic iodide and ethylic oxalate with zinc.

Since then work has been done on this condensation by several chemists, and quite lately by Reformatzky (*Ber.*, 1895, xxviii., 2838), and we have lately employed it with success in preparing the following interesting substances, of which we give a brief account, in order to reserve them for further investigation in the autumn.

(1) $COOC_2H_5 \cdot CH_2 \cdot C(OH)(CH_3) \cdot C(CH_3)_2 \cdot COOC_2H_5$, *ethylic β-hydroxy-ααβ-trimethylglutarate*, is produced by the action of zinc on a mixture of ethylacetoacetate and *ethylic α-bromisobutyrate*, or of *ethylic bromoacetate* and *ethylicdimethylacetoacetate·* It is a thick colourless oil which boils at 165° (35 m.m.), and which, on hydrolysis, is decomposed, with formation of acetic and isobutyric acids. When treated with a mixture of tribromide and pentabromide of phosphorus, it is converted into—

$$COOC_2H_5 \cdot CH_2 \cdot CBr(CH_3) \cdot C(CH_3)_2 \cdot COOC_2H_5,$$

*ethylic β-bromo-ααβ-trimethyl-glutarate*, which distils with slight decomposition at 170—175° (30 m.m.), and, when digested with potassium cyanide in alcoholic solution, is reduced, with formation of—

$$COOC_2H_5 \cdot CH_2 \cdot CH(CH_3) \cdot C(CH_3)_2 \cdot COOC_2H_5,$$

*ethylic ααβ-trimethylglutarate*. This ethereal salt boils at 162° (40 m.m.), and, on hydrolysis, yields *ααβ-trimethylglutaric acid*, a colourless crystalline substance, which melts at 147°.

(2) The ethereal salt of the lactone of *ααβ-trimethyl-β-hydroxyadipic acid.*—

$$COOC_2H_5 \cdot C(CH_3)_2 \cdot \underset{|}{C(CH_3)} \cdot CH_2 \cdot \underset{|}{CH_2}$$
$$O \text{———} CO$$

is produced by distilling the product of the condensation of ethylic levulinate and ethylic bromoisobutyrate. It boils at 187—188° (30 m.m.), and dissolves in ammonia and aqueous potash, being precipitated on the addition of acids unchanged. When hydrolysed with aqueous potash at 0°, it yields the corresponding acid, a colourless crystalline substance, which melts at 105—106°.

(3) Ethylic pyruvate and ethylic β-bromoisovalerate condense readily in the presence of zinc, with formation of *ethylic α-hydroxy αββ-trimethylglutarate,*—

$$COOEt \cdot C(OH)(Me) \cdot CMe_2 \cdot CH_2 \cdot COOEt,$$

a colourless oil, which boils at 160—170° (60 m.m.).

(4) *Ethyl α-methyl-β-hydroxyvalerate,*—

$$Me_2 \cdot C(OH) \cdot CH(Me) \cdot COOEt,$$

is produced by the condensation of ethylic bromopropionate with acetone. It is a colourless oil, which distils at 105° (30 m.m.), and, on hydrolysis, yields the corresponding *α-methyl-β-hydroxyvaleric acid*, a thick colourless syrup, boiling at 160° (35 m.m.). From this acid the following derivatives have been prepared :—

*α-Methyl-β-bromisovaleric acid,*—

$$(CH_3)_2 \cdot CBr \cdot CH(CH_3) \cdot COOH,$$

a white crystalline solid, melting at 79°, and yielding an

oily ethereal salt, which distils in a vacuum almost without decomposition.

*α-Methyl-β-iodoisovaleric acid,*—

$$(CH_3)_2 \cdot CI \cdot CH(CH_3) \cdot COOH,$$
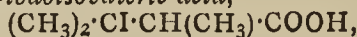
melts at 81°.

*Trimethylacrylic acid,* $(CH_3)_2C:C(CH_3) \cdot COOH$, is formed by the hydrolysis of *ethylic α-methyl-β-bromisovalerate* with alcoholic potash. It crystallises from water in colourless prisms, which melt at 70—71°, and distils without decomposition at 145—150° (50 m.m.). It combines with bromine, readily yielding dibromotrimethylpropionic acid, $(CH_3)_2CBr \cdot CHBr \cdot COOH$, melting at 190°.

99. "*The Electrolysis of the Salts of Monhydroxy Acids.*" By J. WALLACE WALKER, M.A., Ph.D.

An unsuccessful attempt was made to synthesise the alcohols of the glycollic series by electrolysis of strong solutions of the salts of the monhydroxy-acids.

100. "*The Action of Formic Aldehyde on Phenylhydrazine, and on some Hydrazones.*" By J. WALLACE WALKER, M.A., Ph.D.

Beside the already known compound, $(C_6H_5N_2)_2(CH_2)_3$, obtained by the interaction of these substances, the author has prepared a number of others by varying the conditions of the reaction. The relationships of the different substances is fully discussed in the paper.

101. "*The Colouring-matter of Sicilian Sumach, Rhus coriariæ.*" By A. G. PERKIN and GEORGE YOUNG ALLEN.

Sumach, which consists of the dried and powdered leaves of the genus *Rhus*, especially *R. coriaria* (Sicilian) and *R. cotinus* (Venetian sumach), is used in tanning, and also in dyeing and calico-printing, on account of the tannin matter it contains, which according to Löwe is gallotannic acid (Fresenius, *Zeit. Anal. Chem.*, xii., 128). According also to Chevreul it contains a yellow colouring-mattter (Watts, "Dict. Chem.," 1874, v., 614. Löwe (*Zeit. Anal. Chem.*, xii., 127), who examined the different varieties of sumach, stated that they contained quercetin and quercitrin, but this is certainly incorrect as regards Sicilian sumach.

The colouring-matter, $C_{15}H_{10}O_8$, forms glistening yellow needles, having dyeing properties similar to those of quercetin and fisetin, but is distinguished from these by its colour reactions with dilute alkalies. The sulphuric acid compound, $C_{15}H_{10}O_8 \cdot H_2SO_4$, forms orange-red needles, and the acetyl derivative, $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, m. p. 203—204°. Fused with alkali, it yields *phloroglucol* and *gallic acid*. These reactions show it to be identical with *myricetin*, the colouring-matter of *Myrica nagi* (see previous abstract). Sicilian sumach also contains some quantity of free gallic acid.

102. "*The Colouring-matter of Querbracho colorado.*" By ARTHUR G. PERKIN and OSWALD GUNNELL.

The wood of *Querbracho colorado* constitutes the tannin matter "querbracho," which is suitable for the production of Morocco leather, and, moreover, in conjunction with alum, it gives the leather a bright yellow shade, instead of the darker colours prepared in the ordinary way. Jean (*Bull. Soc. Chim.*, xxxiii., 6) found it to contain a tannin differing from those of oak bark and chestnut wood. According to Arnaudon (Watts, "Dict. Chem." viii., 1732) it contains a yellow colouring-matter.

The colouring-matter, $C_{15}H_{10}O_6$, forms glistening yellow needles, dyeing shades similar to those of quercetin, and yielding compounds with mineral acids. The benzoyl derivative, $C_{15}H_6O_6(C_7H_5O)_4$, colourless needles, m. p. 180—181°, and the acetyl derivative,—

$$C_{15}H_6O_6(C_2H_3O)_4,$$
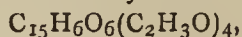
colourless needles, m. p. 196—198°, were prepared. Fused with alkali it yields *protocatechuic acid*, and probably *resorcinol*. Its dyeing properties were identical with those of fisetin, $C_{15}H_{10}O_6$, the colouring-matter of young fustic (*Rhus cotinus*), and there could be little doubt that it was *fisetin*.

A second substance, $C_{14}H_{10}O_{10}$, forming minute prisms,

was also isolated, and was found to be *ellagic acid*, and further, the presence of a considerable quantity of *gallic acid* was detected, these latter being, no doubt, chiefly formed during the isolation of the fisetin from the querbracho.

103. "*On Atisine, the Alkaloid of Aconitum heterophyllum.*" By H. A. D. JOWETT, D.Sc.

The author has investigated the nature and properties of the alkaloid contained in the roots of the non-toxic *Aconitum heterophyllum*. This alkaloid was examined by Broughton in 1873, who named it atisine, and ascribed to it the formula $C_{46}H_{74}N_2O_5$; it was subsequently examined by Wasowicz and by Alder Wright. The powdered roots were extracted by percolation with a mixture of methyl and amyl alcohol, and from this percolate was obtained the crystalline hydrochloride or hydriodide by the method described in the paper.

*Atisine,* for which the author adopts the formula $C_{22}H_{31}NO_2$, could only be obtained as a colourless varnish, soluble in alcohol, ether, or chloroform, slightly soluble in water, and insoluble in petroleum ether. Its alcoholic solution is lævorotatory, $[a]_D = -19 \cdot 6$, and though the base is amorphous it yields a series of crystalline salts.

*Atisine hydrochloride,* $C_{22}H_{31}NO_2 \cdot HCl$, crystallises either from water or from a mixture of alcohol and ether in well-defined prisms, which melt at 296° (corr.) and are freely soluble in water or alcohol, but insoluble in ether. The aqueous solution of the salt is dextrorotatory, $[a]_D = + 18 \cdot 46°$.

*Atisine hydrobromide,* $C_{22}H_{31}NO_2 \cdot HBr$, crystallises from water or a mixture of alcohol and ether, either singly or in rosettes of needles, which melt at 273° (corr.). The salt is freely soluble in water and alcohol, but insoluble in ether or petroleum ether, and in aqueous solution is dextrorotatory, $[a]_D = + 24 \cdot 3°$.

*Atisine hydriodide,* $C_{22}H_{31}NO_2 \cdot HI$, crystallises from hot water or alcohol in well-defined plates or tables, melting at 279—280° (corr.), soluble in hot water or alcohol, but sparingly soluble in cold water. Its aqueous solution is dextrorotatory, $[a]_D = + 27 \cdot 4°$. This salt cannot apparently be prepared by the direct action of hydrogen iodide upon the base, but is easily prepared by precipitating a solution of any salt of atisine with potassio-mercuric iodide, and decomposing the precipitate with hydrogen sulphide.

The *nitrate* (m. p. 252°, corr.) and *platinichloride* (m. p. 229°, corr.) were also obtained as well-defined crystalline salts, but the *aurichloride* could only be obtained as an amorphous powder. The results of the analyses of a number of pure salts led to the adoption of the formula $C_{22}H_{31}NO_2$ for the base.

The hydriodide, when treated with hydrogen iodide, yielded no methyl iodide, and thus the alkaloid was shown to contain no methoxyl groups.

When either the base or its salts are mixed with alkalis or acids in either alcoholic or aqueous solution, no fission of the molecule takes place, but a new base, atisine monohydrate, $C_{22}H_{31}NO_2 \cdot H_2O$, is formed. Neither this base nor any of its salts could be obtained in the crystalline condition, but analyses of the *aurichloride* and *platinichloride* confirmed the formula given above.

A preliminary examination of the physiological action of the *nitrate* by Dr. Cash, F.R.S., showed that the alkaloid is non-toxic, and that its action somewhat resembles aconine.

104. "*The Action of Methyl Alcohol on Aconitine. Formation of Methyl Benzaconine.*" By WYNDHAM R. DUNSTAN, F.R.S., THOMAS TICKLE, and D. H. JACKSON, Ph.D.

When aconitine (or a salt) is heated with methyl alcohol in a closed tube between 120—130°, the alkaloid loses one molecular proportion of acetic acid and takes up one methyl group, forming *methyl benzaconine,*—

$$C_{33}H_{45}NO_{12} + CH_3OH = C_{34}H_{45}NO_{11} + CH_3COOH.$$
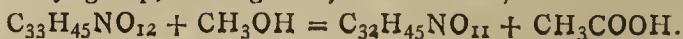
The composition of the new base has been ascertained by combustion, and verified by estimation of the quantity of acetic acid separated in its production from aconitine, by estimation of the amount of benzoic acid separated on hydrolysis, and also by the determination of the number of methoxyl groups present, which has shown that the base contains one more than aconitine.

*Methyl benzaconine* is a well-crystallised base (m. p. 210—211°, corr.), soluble in alcohol ether and benzene, and most readily crystallised by adding light petroleum to its ethereal solution. It forms crystalline salts; the *hydrochloride* and the *hydrobromide* have been examined.

On hydrolysis, methyl benzaconine loses benzoic acid, forming a base which appears to be methyl aconine, but has not so far been completely investigated. Methyl benzaconine produces a well-marked physiological effect when administered to animals, but, unlike aconitine, it is not a powerful poison.

The authors are at present engaged in investigating the mechanism of the remarkable reaction which has led to the formation of this alkaloid, the acetyl group of aconitine being apparently replaced by methyl.

105. "*The Chemical Inactivity of Röntgen Rays.*" By H. B. DIXON and H. BRERETON BAKER.

The authors have investigated the question whether Röntgen rays are able to influence chemical change, either by starting it or by accelerating or diminishing it after it has been started by ordinary light. In all cases examined negative results were obtained. These were carbon monoxide and oxygen (dried and moist), hydrogen and oxygen, hydrogen and chlorine, carbon monoxide and chlorine, hydrogen sulphide and sulphur dioxide, solutions of sodium sulphite and oxygen, slow oxidation of phosphorus, decomposition of hydrogen peroxide.

106. "*Colloidal Chromsulphuric Acid.*" By H. T. CALVERT and T. EWAN.

By heating together one molecular proportion of chromium sulphate and four to six molecular proportions of sulphuric acid at 115° for one or two days, Recoura (*Ann. Chim. Phys.*, 1895, [7], iv., 516) has prepared a series of bodies having the formulæ $Cr_2(SO_4)_3 \cdot 4H_2SO_4$, $Cr_2(SO_4)_3 \cdot 5H_2SO_4$, &c., which he calls chromopolysulphuric acids. These compounds dissolve readily in water, yielding yellowish-green opalescent solutions. The behaviour of these solutions makes it appear probable that the chromosulphuric acids do not exist in them as such, but are hydrolysed, forming a colloidal substance, $Cr_2(SO_4)_3 \cdot H_2SO_4$, and free sulphuric acid. Recoura does not attempt to decide whether this is so or not. Experiments recently made by W. R. Whitney (*Zeit. Physikal, Chem.*, 1896, xx., 59) lead him to the conclusion that the above view is the correct one. The following experiments, which were carried out in part more than a year ago, may be of interest as yielding further evidence in the same direction.

The green opalescent solutions were filtered through porous earthenware (a "Pasteur-Chamberland candle" was used). A dark green gelatinous deposit remained on the outside of the pot; the filtrate was almost colourless, and contained a mere trace of chromium together with the excess of sulphuric acid over and above that required to form the compound $Cr_2(SO_4)_3 \cdot H_2SO_4$. There was thus no doubt that the gelatinous substance removed from the solution possessed this composition; the same body was obtained from acids of the formulæ $Cr_2(SO_4)_3 3H_2SO_4$ and $Cr_2(SO_4)_3 5H_2SO_4$.

The following are the details of the experiments:— Chromium sulphate was prepared by reducing chromic acid with pure alcohol in presence of sulphuric acid (Traube, *Annalen*, 1848, lxvi., 168). It was re-crystallised by precipitating its aqueous solution with alcohol, and dried in a vacuum. On prolonged heating to 200° it lost about .11 mols. of water; a determination of the sulphuric acid, however, showed that its formula was $Cr_2(SO_4)_3 12 \cdot 75H_2O$.

I. One molecule of this salt was mixed with 3 mols. of concentrated sulphuric acid, and the mixture heated to 115—120° for seven days. The mass dissolved readily in water; 10 c.c. of the pale green opalescent solution yielded 0·0596 grm. $Cr_2O_3$ and 0·5177 grm. $BaSO_4$. The liquid was then filtered through the moist porous pot by evacuating the latter internally; the first portion of the filtrate was rejected. Since the filtration was very slow the filtrate probably became somewhat too concentrated by evaporation. 10 c.c. of the filtrate gave 0·1674 grm. $BaSO_4$. The solution therefore contained—

$$Cr_2(SO_4)_3 + 2 \cdot 68H_2SO_4,$$
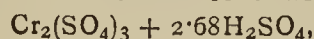
and the filtrate contained $Cr_2(SO_4)_3 + 1 \cdot 84H_2SO_4$. The composition of the gelatinous compound was—

$$Cr_2(SO_4)_3 \cdot 0 \cdot 84H_2SO_4.$$
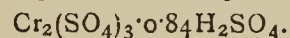
II. This experiment was made in the same way, the results being :—The original solution contained—

$$Cr_2(SO_4)_3 + 5 \cdot 00H_2SO_4;$$
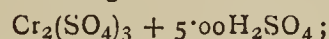
the filtrate contained $Cr_2(SO_4)_3 + 4 \cdot 25H_2SO_4$. The substance removed was thus $Cr_2(SO_4)_3 + 0 \cdot 75H_2SO_4$.

The formation of the colloidal substance was not observed when one molecular proportion of chromium sulphate was heated with one molecular proportion of sulphuric acid for two weeks.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 6, August 10, 1896.

**The Lavoisier Memorial.**—A list is inserted of the subscriptions given by learned bodies and private individuals for the proposed monument. The Chemical Society of London has contributed 625 frcs.; the Royal Society of Dublin, 500; and Trinity College, Dublin, 676 frcs. The total hitherto received is 47553·30 frcs. A further subscription is in progress, which is headed by the Emperor of Russia with 2000 roubles. The execution of the statue will be entrusted to M. Barras.

**Researches on Cyanic Acid.**—M. Berthelot.—A collection of thermo-chemical data. It appears that the transformation of ammonium cyanate into urea is attended with a disengagement of $+8 \cdot 3$ cal.

**Researches on the Volatility of Levulic Acid.**—MM. Berthelot and André.—The point of ebullition of levulic acid is 239°. Levulic acid tends to be split up into two portions, differing in composition. The most volatile portion, forming about the half of the total product, corresponds to the formula $C_5H_8O_3\frac{1}{2}H_2O$. The residue is $C_5H_{10}O_4$ (dioxyvaleric acid).

**Reactions exerted in the Cold between Phosphoric Acid and Ether in presence of Water. Coefficient of Distribution.**—M. Berthelot and G. André.—Setting out with an acid of 0·434 grm. per c.c., an aqueous solution of phosphoric acid gives up merely an insignificant quantity of acid to the ether with which it is agitated.

**Part Played by the Dielectric in the Discharge of Röntgen's Rays.**—Jean Perrin.—This paper requires the two accompanying figures.

No. 7, August 17, 1896.

**On the Copper Mines of Sinai, worked by the Ancient Egyptians.**—M. Berthelot.—The copper mines of Sinai are the most ancient of which history makes mention. According to authentic documents, they were worked since the time of the Egyptian dynasty (about

5000 years B.C.) until the end of the Ramesseïdes (about 1300 to 1200 B.C.). Their possession had been the object of several wars, but they had been abandoned for 3000 years, on account of the poverty of the ores. It was from these mines that was obtained the sceptre of Pepi I., a king of the VI.th dynasty. This sceptre, made of pure copper, of which I have made an analysis, is preserved in the British Museum. The adits still exist, as well as the ruins of the furnaces, the crucibles, the huts of the miners, and some fragments of their tools. In the specimens obtained by M. de Morgan there occur three ores : turquoise, copper hydrosilicate, and sandstones impregnated with copper. These actual ores are superficial, and form a cap, derived from the alteration of deeper pyritic beds which the ancient miners failed to reach. The turquoises contained 3·32 per cent cupric oxide ; the cupriferous gritstones are equally poor. Among the débris have been found fragments of furnaces and crucibles, slags, and cinders, fragments of tools. Nor is there evidence of the use of fluxes. Some of the fragments of tools contain arsenic, which was used by the Greek and Egyptian alchemists for hardening copper. It is interesting to note that metallurgical procedures similar to those of our days had been reached empirically 7000 years ago.

**Combination of Argon with Water.**—P. Villard.— Argon combines with water to form a crystalline and dissociable hydrate analogous to the hydrates of gases already known, and taking rise under similar conditions. The argon being compressed to about 150 atmospheres in presence of water kept near upon 0°, it is sufficient to refrigerate a point of the tube so as to congeal at this point the water which moistens the sides of the tube, when there is produced a crystallisation which sets out from the refrigerated point. At 0° the tension of dissociation of argon hydrate is about 105 atmospheres. At $+8°$ it reaches 210 atmospheres.

## ADDRESS TO STUDENTS.

THE present position and prospects of chemical science justify a few words of advice to students.

Discoveries have been lately made of a novel character, such as may possibly modify the course of future research. Thus it is very probable that argon and helium are not merely isolated bodies hitherto unknown, but that they are the types of a new class of elements which may seriously modify our general views. Hence they must require careful examination from every conceivable point of view. Technically, indeed, these elements may be of little direct moment, but their indirect bearings may be for the present beyond our ken.

The grand question of the elements as modifications of protyle, or as mere desultory and ultimate essences, has not been advanced any nearer to a definite solution, but our suspicions of their modifiable character are certainly becoming more justified. Young chemists who have time at their disposal might very advantageously employ it in this direction. The failure of Dr. S. Brown to effect a mutual conversion of carbon and silicon should not, we think, discourage us from future attempts in this direction.

A recent discovery has made us acquainted not indeed with a new form of matter, but—what is certainly of not less importance—a new modification of energy. The X rays of Prof. Röntgen have indeed proved of practical value, more than sufficient to compensate for the foolish jests which they have supplied to the literary and general papers. But higher than their value, as placing at our disposal a new analytical procedure, must rank the prospect which they hold out to us of reaching other kinds of vibrations not yet realised.

It seems that the advance which we have already accomplished in chemical and physical science, instead of narrowing, actually expands the fields which remain for us to occupy. If Science means the interpretation of the universe, its scope must widen with our comprehension of the almost infinite nature of its task. The recent collapse of China, which obstinately closed its eyes to the extension of knowledge and insisted on grovelling amidst the relics of the past, ought to be for us a final lesson.

# UNIVERSITIES AND COLLEGES.

## UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must have passed the Matriculation Examination. No exemption from this rule is allowed on account of Degrees obtained or Examinations passed at any other University. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, and Medals depending upon them, are open to Women upon exactly the same conditions as to Men.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June.

The Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine. These Examinations may be held not only at the University of London, but also, under special arrangement, in other parts of the United Kingdom, or in the Colonies.

Every candidate for the Matriculation Examination must, not less than five weeks before the commencement of the Examination, apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the commencement of the Examination, accompanied by a Certificate showing that the candidate has completed his sixteenth year, and by his Fee for the Examination. As no candidate can be admitted after the List is closed, any candidate who may not have received a Form of Entry within a week after applying for it must communicate immediately with the Registrar, stating the exact date of his application and the place where it was posted.

Every candidate entering for the Matriculation Examination for the first time must pay a Fee of £2 to the Registrar. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him, but he shall be allowed to enter for any subsequent Matriculation Examination upon payment, at every such entry, of an additional Fee of £1, provided that he comply with the Regulations in the preceding paragraph.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages : — Greek, French, German, Sanskrit, or Arabic. The English Language, and English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements ; including their compounds, their chief physical and chemical characters, their preparation, and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years ; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years ; and the third will receive an Exhibition of fifteen pounds per annum for the next two years ; such exhibitions are payable in quarterly instalments provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money ; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

### INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the third Monday in July.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

#### Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

### B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the third Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

#### Examination for Honours.

The examination for Honours in Chemistry will take place on Monday, Tuesday, and Wednesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday and Wednesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

### DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Every candidate for this Degree must state in writing the special subject within the purview of the Faculty of Science, as set out in the Programme of the B.Sc. Examination, upon a knowledge of which he rests his qualification for the Doctorate; and with this statement he shall transmit an original Dissertation or Thesis (at least six copies), printed, type-written, or published in his own name, treating scientifically some special portion of the subject so stated, embodying the result of independent research, or showing evidence of his own work, whether conducted independently or under advice, and whether based on the discovery of new facts observed by himself, or of new relations of facts observed by others, or, generally, tending to the advancement of Science. Every candidate may further specify any printed contribution or contributions to the advancement of Science which he has at any time previously published. If the Dissertation or Thesis be approved by the Examiners, the candidate shall be required to present himself at the University upon such day or days within the first twenty-one days of June as may be notified to him, and shall, at the discretion of the Examiners, be further tested, either orally or practically, or by printed questions or by all of these methods, with reference both to the special subject selected by him and to the Thesis.

### PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination. Not less than five weeks before the commencement of the Examination he must apply to the Registrar for a Form of Entry, which must be returned not less than four weeks before the Examination, accompanied with the candidate's fee.

The Fee for this examination is Five Pounds.

## UNIVERSITY OF OXFORD.

*Wayflete Professor of Chemistry*—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

*University Laboratory.*—Demonstrators, W. W. Fisher, V. H. Veley, F.R.S., J. E. Marsh.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

*Christ Church Laboratory.*—A. Vernon Harcourt, F.R.S.

*Balliol Laboratory.*—Sir J. Conroy, F.R.S., D. H. Nagel.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

## UNIVERSITY OF CAMBRIDGE.

*Professor of Chemistry*—G. D. Liveing, M.A., F.R.S.

*Jacksonian Professor of Natural and Experimental Philosophy*—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in the first or third term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science in King's, Trinity, St. John's, St. Peter's, Clare, Trinity Hall, Queen's, Jesus, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in November, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar.*

## UNIVERSITY OF DUBLIN.
### TRINITY COLLEGE.

*Professor of Chemistry*—J. Emerson Reynolds, D.Sc., M.D., F.R.S.

*Assistant Lecturer*—Emil A. Werner, F.C.S., F.I.C.

*Demonstrator*—J. Percy Bailey, B.A.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The Laboratories will open on the 1st of October. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered :—

1. *Inorganic Chemistry and Chemical Philosophy.* — Elementary, first year ; advanced, second year.
2. *Organic Chemistry.* — General, second year ; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

*The Summer Course of Practical Chemistry for Medical Students* begins during the first week in April and terminates with the first week in July.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

### KING'S COLLEGE.
#### (DIVISION OF ENGINEERING AND APPLIED SCIENCE).

*Professor of Chemistry*—J. M. Thomson, F.R.S.E., F.C.S.

*Demonstrator of Practical Chemistry*—Herbert Jackson, F.C.S.

*Assistant Demonstrators*—P. H. Kirkaldy, F.C.S., and W. H. Sodeau.

The Academical Year consists of Three terms. The days fixed for the Admission of New Students in the Academical Year 1896-97 are Tuesday, September 29, Wednesday, January 20, and Wednesday, April 28.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts ; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

*Second Year.*—Students attend in the Laboratory twice a week, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis. Any Student of this Division may be admitted to this Class at any period of his study on payment of an extra fee.

*Experimental and Analytical Chemistry in the Laboratory.*—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator ; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od. ; per ann., £8 8s. od. ; Practical Chemistry per term, £4 4s. od. ; per ann., £10 10s. od. ; Experimental and Analytical Chemistry—Daily attendance : One month, £4 4s. ; Three months, £10 10s. ; Six months, £18 18s. ; Nine months, £26 5s. Three days a week : One month, £2 12s. 6d. ; Three mos., £6 6s. ; Six mos., £11 11s. ; Nine mos., £15 15s.

#### METALLURGY.

*Professor*—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures : The Selection and Economic Preparation of Fuel and of Refractory Materials ; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

#### PHOTOGRAPHY.

*Lecturer*—Prof. J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students will be afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

#### EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

### UNIVERSITY COLLEGE.
#### FACULTY OF SCIENCE.

*Professor*—William Ramsay, Ph.D., F.R.S.

*Assistants*—Morris Travers, B.Sc., Alexander Kellas, B.Sc., and J. W. Walker, B.Sc., Ph.D.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Wednesday, October 6th, until Friday, December 18th ;

Second Term, from Tuesday, January 12th, 1897, till Friday, April 2nd ;

Third Term, from Tuesday, April 27th, till Friday, July 2nd. Class Examinations begin on June 21st.

*Junior Courses.*

First Term : Tuesday, Thursday, and Saturday at 10. Second and Third Terms : Tuesday, Thursday, and Saturday at 10, Friday at 4. Fee :—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

*Senior Course of Chemistry.*

First and Second Terms : The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fees :—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Int. Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

### Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9, beginning on January 14. The hour will be altered by special arrangement with the class if necessary.

Fee :—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

### Organic Chemistry.

Tuesday, Thursday, and Saturday, at 9, in the First Term ; Tuesday, Thursday, and Saturday, at 10, in the Second Term ; and Tuesday and Thursday at 9, and Saturday at 11, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who are studying the subject from a scientific standpoint. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course besides the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours ; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee :—For the Course, £6 6s. ; for the Second and Third Terms, £4 14s. 6d. ; for a Term, £2 12s. 6d. ; for a Second Course, £3 3s.

### Junior Practical Class.

First and Second Terms, Tuesday and Thursday, at 11.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

### Senior Practical Class.

Wednesdays from 2 to 4 and Saturdays from 10 to 12 during the Third Term ; also Tuesdays and Thursdays from 11 to 12.

Fee :—(Including cost of materials) £5 5s. ; for a Second Course, £3 3s.

### Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees : for the Session, £26 5s. ; six months, £18 18s. ; three months, £10 10s. ; one month, £4 4s.

Three specified days a week :—for the Session, £15 15s.; six months, £11 11s. ; three months, £6 6s. ; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London :—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Lectures on Chemical Technology may acquire here the requisite knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1896-97 ; also the Clothworker's Scholarship of £30.

## ROYAL COLLEGE OF SCIENCE AND ROYAL SCHOOL OF MINES.

*Professor*—W. A. Tilden, D.Sc., F.R.S.
*Assistant Professor*—W. P. Wynne, D.Sc., F.R.S.
*Demonstrators*—H. Chapman Jones and J. W. Rodger, A.R.C.S.
*Assistants*—G. S. Newth, A. Eiloart, Ph.D., B.Sc., and M. O. Forster, Ph.D.

The Royal College of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is incorporated with the Royal College of Science. Students entering for the Associateship of the Royal School of Mines obtain their general scientific training in the Royal College of Science. The instruction in the Royal College of Science is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Royal College of Science, or of the Royal School of Mines. Students who are not candidates for the Associateship are permitted to enter as occasional students in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Royal College of Science is given in one or more of the following divisions :—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins on the 7th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidates being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and in the third year those of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table :—

| | Lectures.<br>£ | Laboratory.<br>£ |
|---|---|---|
| Chemistry | 3 | 13 |
| Physics | 5 | 12 |
| Biology with Botany | 5 | 12 |
| Geology with Mineralogy | 4 | 8 |
| Mechanics | 4 | 6 |
| Metallurgy | 2 | 13 |
| Mining | 4 | |
| Astronomical Physics | 2 | 3 |

Agricultural Chemistry, per term, £13. Mathematics and Mechanical Drawing, £3 per term. Model and Free-hand Drawing, £1 per term. Descriptive Geometry, £3 per session. Mine Surveying, £10.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half fees.

Associates of the Royal College of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

*Bona fide* teachers qualified to earn payments for teaching Science according to the rule of the Science and Art Directory may obtain permission to attend free any course of lectures.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

*Summer Courses for Teachers.*—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 250 teachers are admitted to them, and they receive third class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science and Art Directory.)

*Working Men's Lectures.*—Notification of these will be given in the newspapers.

## THE SCHOOL OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Fifty-fifth Session will commence on Monday, October 5th, 1896.

*Professors*—Chemistry, J. Norman Collie, Ph.D., F.R.S.; Botany, J. Reynolds Green, Sc.D., F.R.S., F.L.S.; Materia Medica and Pharmacy, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies.

Prospectuses and further information may be obtained from Mr. Richard Bremridge, Secretary and Registrar, 17, Bloomsbury Square, London, W.C.

## UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.
### UNIVERSITY OF WALES.

*Professor* — H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

*Assistant Lecturer and Demonstrator*—A. W. Warrington, M.Sc. (Vic.), F.I.C.

*Lecturer in Agricultural Chemistry*—J. Alan Murray, B.Sc. (Edin.).

The College is open to male and female students above the age of sixteen years. The Session commences on Tuesday, September 29, on which day all Students will be expected to meet the Professors in the Library of the College.

*Lecture Courses.*—(1) Matriculation Course; three lectures weekly during the Michaelmas and two weekly during the Lent and Easter Terms. (2) Intermediate Science Pass Course; four lectures weekly during the Lent and Easter Terms. (3 and 4) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, two lectures weekly on Chemical Theory. (Courses A and B will generally be given in alternate Sessions; for 1896-7, Course A.) (5 and 6) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly throughout the Session.

*Laboratory Courses.*—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2.15 to 5 p.m., except on Wednesdays and Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

*Fees.*—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

*Scholarships and Exhibitions* varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

The Chemical Laboratories in connection with this College have been recently built, and are fitted with every convenience for the prosecution of chemical studies.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

## UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.
### A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

*Chemistry.*—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, Fred. Marsden, Ph.D., B.Sc. Assistant Lecturer in Agricultural Chemistry, F. V. Dutton.

*Physics.* — Professor, Andrew Gray, M.A., LL.D., F.R.S.

The Session opens September 29th, 1896. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

*Matriculation Course.*—Subjects: Those prescribed for the Matriculation Examination of the University of Wales. Fee for the Term £2 2s. A class for revision of

Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

*Intermediate Course.*—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Term £2 2s.

*B.Sc. Course.*—Organic Chemistry. Fee for the Session, £3 3s.

*Medical Course.*—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

*Agricultural Chemistry.*—Fee, £2 2s.

*Laboratory Courses.*—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and students can make one *Annus medicus* at the college. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

## UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

*Professor*—C. M. Thompson, M.A., D.Sc., F.C.S.

*Demonstrators*—E. P. Perman, D.Sc., F.C.S., and A. A. Read, F.I.C., F.C.S.

The Session commences October 15th, and terminates on June 23rd, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course, and is the qualifying course for the Intermediate Examination of the University of Wales. Together with laboratory practice, it will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B.) Examination of the University of London. Fee, £4 4s.

The Senior Course consists of some 60 lectures devoted to Physical and Theoretical Chemistry; Fee, £3 3s.

A course of 20 lectures on Qualitative Analysis and a short course on Organic Chemistry will also be given.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales

and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

## UNIVERSITY COLLEGE, BRISTOL.

*Professor of Chemistry*—Sydney Young, D.Sc., F.R.S.

*Lecturer*—Francis E. Francis, B.Sc., Ph.D.

*Junior Demonstrator*—E. Halford Strange, B.Sc.

The session 1896-97 will begin on October 6th. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Secretary.

### DAY LECTURES.

#### *Inorganic Chemistry.*

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

*Junior Course.*—Two Lectures a week will be given during the First and Second Terms. Fee, £3 3s.

*Senior Course.*—Three Lectures a week will be given throughout the Session. Fee, £5 5s. There will be tutorial classes in connection with the Junior and Senior Courses.

*Advanced Course.*—One Lecture a week will be given throughout the Session. Fee, £2 12s. 6d.

#### *Organic Chemistry.*

This Course will relate to the more important groups of the Compounds of Carbon.

Two Lectures a week will be given during the Second Term, and three Lectures a week during the Third Term. Fee, £3 3s. An advanced course of lectures will also be given one day a week during the session. Fee, £2 12s. 6d.

#### *Practical Chemistry.—Laboratory Instruction.*

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it will be closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

| | 5 Days a Week. | 4 Days a Week. | 3 Days a Week. | 2 Days a Week. | 1 Day a Week. |
|---|---|---|---|---|---|
| Per Session .. .. | 15 | 12½ | 10 | 7½ | 5 |
| „ Two Terms .. | 11 | 9 | 7½ | 5½ | 3½ |
| „ One Term .. | 7 | 6 | 4½ | 3½ | 2½ |

Students may arrange to divide their days of laboratory work into half-days.

*Chemical Scholarship.*—Among others, a Chemical Scholarship of £25 is offered for competition.

### EVENING LECTURES.

Two courses of Lectures will be delivered during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic and Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures. Fee for each course, 7s. 6d.

*Practical Chemistry — Laboratory Instruction.* — The Laboratory will be open on Tuesday and Thursday evenings from 7 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees :—(Two Terms) Two Evenings, 25s.; One Evening, 15s. (One Term) Two Evenings, 15s.; One Evening, 10s 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4½d.), containing detailed information of the various Courses, may be obtained on application to the Secretary.

### MASON COLLEGE, BIRMINGHAM.

*Professor*—Percy F. Frankland, Ph.D., B.Sc., F.R.S.
*Assistant Lecturer*—C. F. Baker, Ph.D., B.Sc.
*Demonstrator*—(Vacant).
The Session will be opened on October 5th, 1896.

#### Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. Lecture days—Wednesdays and Fridays at 11.30.

Persons entirely unacquainted with Chemistry are recommended to attend this Course before entering for the General Course. Candidates for the Matriculation Examination of the University of London also are advised to attend this Course.

#### General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays from October to December, and on Mondays, Tuesdays, and Wednesdays from January to March, at 9.30 a.m. A Tutorial Class is held in connection with this Course once a week throughout the Session. Fee, £5 5s. for the course.

2. May to July (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Wednesday, and Friday at 12 noon Fee, £1 11s. 6d.

The General Course (including Inorganic and Organic lectures) qualifies for graduation in the medical faculties of the universities of Edinburgh, Glasgow, Aberdeen, and Durham.

Special Courses of Lectures and of Laboratory Instruction are given for Medical Students preparing for the Conjoint Board Examinations.

#### Advanced Course.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet twice a week. Fee for the session £3 3s.

#### Laboratory Practice.

The College Laboratory is open daily from 9.30 to 5, except on Saturdays, when it is closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees :—

| | All day. | Three hours per day. |
|---|---|---|
| One Term .. .. .. | 7 guineas .. .. | 4½ guineas. |
| Two Terms .. .. | 13 „ .. .. | 8½ „ |
| Three Terms .. .. | 18 „ .. .. | 12 „ |

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

#### Metallurgy.

Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each of the first two courses, and for each of the two sections of the third course. A more advanced course of about sixty lectures upon selected subjects is also given by Mr. McMillan, the Lecturer in Metallurgy.

There is a separate laboratory for metallurgical students in which provision is made for instruction in assaying, &c

#### Evening Classes.

Special Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

#### Scholarships.

*Priestley Scholarships.*—Three Open Scholarships in Chemistry of the value of £100 each are awarded annually in September.

*Bowen Scholarship.*—One Open Scholarship in Metallurgy of the value of £100 is awarded annually in September.

*Forster Research Scholarship.*—A Scholarship of the value of £50 is annually awarded.

For particulars apply to the Registrar.

#### Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturer.

## BRADFORD TECHNICAL COLLEGE.

### CHEMISTRY AND DYEING DEPARTMENT.

*Professor*—W. M. Gardner, F.C.S.
*Demonstrator*—A. B. Knaggs, F.C.S.
*Lecturer on Botany and Biology*—William West, F.L.S.

The school year is divided into three terms. The Session commences on September 14th and terminates on July 17th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Fee, £4 per Term, or £11 per Session.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

## ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

### CHEMICAL DEPARTMENT.

*Professor*—Prof. E. Kinch, F.C.S., F.I.C.
*Assistants*—Cecil C. Duncan, F.I.C., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

## VICTORIA UNIVERSITY. THE YORKSHIRE COLLEGE, LEEDS.

*Professor of Chemistry*—Arthur Smithells, B.Sc. Lond., F.I.C.
*Lecturer in Organic Chemistry*—Julius B. Cohen, Ph.D., F.I.C.
*Assistant Lecturer in Agricultural Chemistry*—Herbert Ingle, F.I.C.
*Demonstrator*—Frankland Dent, B.Sc.

The Session begins October 6, 1896.

### Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.
2. Inorganic Chemistry.—First year Honours Course, Non-metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.
3. Inorganic Chemistry. — Second year Honours Course, Metals. Tuesday, Thursday, and Saturday at 9.30 a.m. Fee, £3 13s. 6d.
4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.
5. Organic Chemistry Honours Course.— Wednesday and Friday at 12 noon. Fee, £2 12s. 6d.
6. Theoretical Chemistry.—Advanced Course. Tuesdays and Thursdays at 9.30 a.m. Fee, £2 12s. 6d.

7. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.
8. Agricultural Chemistry.—Monday, Tuesday, and Friday, at 3 p.m., during first and second terms.
9. Chemistry for Teachers.—Saturdays from 9.30 to 12.30 in the first and second terms. Fee, £4 4s.

### Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

*Class in Practical Chemistry*, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

*Practical Chemistry for Medical Students.*—Tuesdays, 9.30 to 11.30 October to end of December; Thursdays, 2 to 4 from January to end of March.

*Practical Course in Sanitary Chemistry.*—At times to be arranged.

*Practical Organic Chemistry for Medical Students.*—At times to be arranged.

### Evening Class.

A Course of twenty Lectures by Mr. Ingle, on the Chemistry of Engineering will begin during the first and second Terms. Fee, 10s. 6d.

### Dyeing Department.

*Professor*—J. J. Hummel, F.I.C.
*Lecturer and Research Assistant* — A. G. Perkin, F.R.S.E.
*Assistant Lecturer*—W. M. Gardner.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c.

### Leather Industries Department.

*Professor*—H. R. Procter, F.I.C.

The full Course, which extends over a period of three years, is suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and is recommended to sons of tanners. The Course includes instruction in chemistry, engineering, leather manufacture, and practical work in the Leather Industries Laboratory.

### Agricultural Department.

*Professor*—James Muir.

The full Course occupies two years, and includes instruction in chemistry, physics, botany, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture.

Research Students are admitted to the College Laboratories on reduced terms.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition, and one of the 1851 Exhibition Scholarships. The West Riding County Council Scholarships are tenable at the Yorkshire College.

## UNIVERSITY COLLEGE, LIVERPOOL.

*Professor*—J. Campbell Brown, D.Sc.
*Lecturer on Organic Chemistry* — C. A. Kohn, B.Sc., Ph.D.
*Lecturer on Metallurgy*—T. L. Bailey, Ph.D.
*Demonstrators and Assistant Lecturers* — T. L. Bailey, Ph.D., C. A. Kohn, B.Sc., Ph.D., S. B. Schryver, B.Sc., Ph.D., and A. W. Titherley, B.Sc., Ph.D.
*Assistant*—H. H. Froysell.

The Session commences October 5th.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or

for the M.Sc. or D Sc. Degree in Victoria University ; for Degrees in Medicine of Victoria, London, and Edinburgh ; for the Pharmaceutical Diplomas ; for a special Technological Certificate of University College ; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

*Lecture Courses.*

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, £4.

Dental Course, Lectures and Practical. Fee, £5 5s.

Course A.—Non-metals. Fee, £3 10s.

Course B.—Metals. Fee, £3 10s.

Course C.—Organic Chemistry. Fee, £3 10s.

Course H.—Special Organic Subjects. Fee, £1.

Course D.—Physical Chemistry. One Term. Fee, £1.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy. Three Terms. Fee, £2.

Courses F.—Technological Chemistry and Metallurgy : Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper, Iron, and Steel. (3) Lead, Silver and Gold, Aluminium, and other Metals. (4) Distillation of Coal and Tar Industries. (5) Fuel and Gas. (6) Chemistry Applied to Sanitation. (7) Technical Gas Analysis. Three terms. Fee, each course £1 10s.

*Practical Classes.*

(1) Junior. (2) Intermediate : Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Revision Class. (4) Senior : Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Saitanry subjects, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class : Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

*Chemical Laboratory.*

The Chemical Laboratories provide accommodation for every kind of chemical work.

An additional metallurgy room with furnaces has been built, and an Electrochemical department has been added.

The William Gossage Laboratory will be opened during the winter of 1896. This consists of a large and well-fitted general Laboratory for advanced Students, a new gas analysis room, an additional lecture-room for Metallurgy and other classes, and an addition to the Research Laboratory. New stores for students' apparatus and chemicals will be opened in October.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

TABLE OF FEES.

| Per Week. | One Term, Three Months. | Three Terms, One Session. |
|---|---|---|
| One day | £4 | £8 |
| Two days | 6 | 10 |
| Three days | 8 | 12 |
| Four days | 9 | 15 |
| Whole week | 10 10s. | 21 |

Pharmaceutical Course, £11.

*Technological Curriculum.*

*Preliminary Year.*—Chemistry, the Elementary Course. Practical Classes 1 and 2. Mathematics, or Mechanics, or Physics. Elementary Engineering, Drawing, and Design (in this or one of the following years). German.

Or the Victoria Preliminary Course and Examination may be taken.

*First Year.*—Chemistry—Courses A and B ; Chemical Laboratory three days per week; Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work, one day per week. Mathematics (intermediate). German. Engineering, First Year Course, Autumn and Lent Terms. Intermediate B.Sc. Examination may be passed.

*Second Year.*—Chemistry, Lecture Course C, on Organic Chemistry, Lecture Course E or D, Technological Chemistry, Course F, on Metallurgy. Chemical Laboratory, four pays per week. Engineering, Mathematics, or Physics (Advanced). The Final Examination for the Victoria B.Sc., or the Intermediate Examination of the Institute of Chemistry, may be taken.

*Third Year.*—Courses D, F, and C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. The Final Examination for the Associateship of the Institute of Chemistry of Great Britain and Ireland may be taken. Three years study after passing the Preliminary Examination of Victoria University are required for the B.Sc. Degree in the Honours School of Chemistry.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1895, on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

*Evening Classes.*

Classes, including laboratory work, will be held on Metallurgy and on Analysis of Gases.

The Prospectus containing full particulars may be obtained from the Registrar, University College, Liverpool.

## DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

*Professor of Chemistry*—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

*Lecturer in Chemistry*—Saville Shaw, F.C.S.

*Lecturer in Agricultural Chemistry*—R. Greig Smith, B.Sc. (Edin.), F.C.S.

*Assistant Lecturer and Demonstrator*—F. C. Garrett, M.Sc., F.C.S.

The Session will commence on September 28th, 1896.

1. *General Course.* — This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. A section of this Course will be devoted to an outline of Organic Chemistry. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7th. Fee, £3 10s. for the Session.

2. *Advanced Course.*—Inorganic Chemistry, Tuesdays 3 to 4 p.m., during the Session. Fee, £2 ; or for students taking Organic Chemistry, £1.

3. *Organic Chemistry.* — A Course of Lectures will be given throughout the Session, the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a.m., and Fridays 3 to 4 p.m., and will commence on Thursday, October 8th. Fee, £3 10s. for the Session.

Advanced Classes will be formed for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m.

*Metallurgy and Assaying.*—Lecturer, Saville Shaw, F.C.S. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry-Assaying, and in the preparation and analysis of Alloys, &c. Fee as for Chemical Laboratory.

*Agricultural Chemistry.*—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10.

*Practical Chemistry.*—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £2 10s. per term, £6 per session; one day per week, £1 10s. per term, £3 10s. per session.

*Courses of Study.*—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

*Associateship in Physical Science.*—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in—Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year. Associates in Science are admissible one year after obtaining the title of Associate to examination for the degree of Bachelor of Science of the University of Durham.

*Exhibitions.*—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Monday, September 28th.

*Evening Lectures.*—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

## OWENS COLLEGE,
## VICTORIA UNIVERSITY, MANCHESTER.

*Professor and Director of the Chemical Laboratory*—Harold B. Dixon, M.A., F.R.S.

*Professor of Organic Chemistry*—W. H. Perkin, Ph.D., F.R.S.

*Demonstrators and Assistant Lecturers*—George H. Bailey, D.Sc., Ph.D.; Arthur Harden, M.Sc., Ph.D.; P. J. Hartog, B.Sc.; B. Lean, B.A., D.Sc.; and E. Haworth, B.Sc.

*Lecturer in Technical Organic Chemistry*—Dr. J. Thorpe.

*Assistant Lecturer in Metallurgy*—(Vacant).

The Session begins on October 6, 1896, and ends on July 3, 1897.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

### Chemistry Lecture Courses.

*General Chemistry Course.*—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

*Introduction to Organic Chemistry.*—Wednesdays and Fridays, at 9.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

*First Year Honours Course.*—Mondays, Wednesdays, and Fridays, 11.30 a.m., during the two Winter Terms. The Non-Metals.

*Second Year Honours Course.*—Mondays, Wednesdays, Fridays, 3.30 p.m., during the two Winter Terms. The Metals.

*Third Year Honours Course.*—At times to be arranged. Physical Chemistry.

*Organic Chemistry (General).*—Tuesdays and Thursdays, 9.30, during two Winter Terms.

*Organic Chemistry (Honours).*—Mondays and Fridays, 9.30, during the two Winter Terms.

*History of Chemistry and Chemical Philosophy.*—Wednesdays, 10.30, during the Session.

METALLURGY.—*Lectures*: The Metallurgy of Copper, Lead, Silver, Gold, and the Metallurgy of Iron and Steel will be given in alternate years. *Practical*: Saturdays, 9.30.

The Chemical Laboratories are open daily from 9.30. a.m. to 4.30 p.m., except on Saturdays, when they are closed at 12.30 p.m.

*Courses for B.Sc. Degree.*— To qualify for the B.Sc. Degree of the Victoria University, Students have to attend a prescribed course of study extending over three years, and to pass the Preliminary Examination of the University either on entering or at the end of a year's Course.

The Honours Course of Chemistry is as follows:—First year: First year Honours Lectures; Mathematics (3 hours a week); Physics (3 hours a week); a Language (3 hours a week); Chemical Laboratory (3 days per week). Second year: Second year Honours Lectures; General Organic Lectures; Applied Chemistry Lectures; Physics Laboratory (1 day per week); Chemical Laboratory (3 days per week). Third year: Third year Honours Lectures; Honours Organic Lectures; History of Chemistry Lectures; Chemical Laboratory (5 days per week).

The following awards are made to successful Students in the Honours Examination:—A University Scholarship of £50; a Mercer Scholarship of £25. A University Fellowship of £150 is awarded annually among the Graduates in Science for the encouragement of Research. Among the *College* Scholarships open to Chemical Students are the Dalton Chemical Scholarship, £50 per annum for two years; the 1851 Exhibition Scholarship; the John Buckley Scholarship; &c.

### Applied Chemistry.

*First Course.*—Sulphuric Acid and Alkali Manufactures. General Principles of Chemical Engineering.

*Second Course.*—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

*Third Course.*—Natural and Artificial Dye-stuffs, and the Principles of Dyeing and Printing.

### Certificates in Applied Chemistry.

The course extends over a period of three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

Before admission to the first year's course students are required to give such evidence of elementary knowledge of Mathematics and Chemistry as shall be considered satisfactory by the Senate.

The first year's course is the same for all students working for the certificate.

In the second and third years a choice may be made between Inorganic and Organic Chemistry. By this division of the subject a student wishing to apply himself specially to the inorganic side of the science, may attend during his second year the Honours course in Metals, and courses on Geology or Mineralogy, and during his third year, courses on Metallurgy and on Geology or Mineralogy; while a student wishing to apply himself specially to the organic side of the science, may attend during his second and third years the Courses on Organic Chemistry, and courses on the Coal Tar Colours and on Dyeing and Printing.

Part of the Laboratory practice in the second and third years will consist in the examination and analysis of raw materials, products from chemical works, &c., in connection with the special courses of lectures on Applied Chemistry. In the Chemistry and Physical laboratories the practical work in the second year will be arranged in accordance with the branch of Chemistry selected by the candidate.

In the third year the student, if sufficiently advanced, will be set to work on some analytical process or problem in Applied Chemistry, under the direction of the teaching staff.

## UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.
*Professor of Chemistry*—Frank Clowes, D.Sc. Lond., F.I.C.
*Demonstrators of Chemistry*—J. J. Sudborough, D.Sc., Ph.D., F.I.C.; R. M. Caven, B.Sc., F.I.C.; and G. Melland, B.Sc., A.R.S.M., F.I.C.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences on Monday, September 28th.

*Lecture Courses.*—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms. In his third year he attends a course on Advanced Organic Chemistry or Applied Chemistry. Fee for Day Lectures and Classes: Non-Metals or Metals 42s.; Organic Chemistry (one term) 21s.; Advanced Organic Chemistry, 21s. per term.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 5s.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

*Practical Chemistry.*—The chemical laboratory is open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for two hours per week, three hours 15s., four hours 20s., six hours 30s., per term.

*Courses of Technical Chemistry Lectures* are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

*Pharmaceutical Students* can at all times work in the Chemical Laboratory, taking work suitable for the preparation for the Minor Examinations. Special lectures will also be given in Chemistry and Materia Medica.

*Government Lectures and Classes.*—Evening Lectures and Laboratory instruction will be given by the Demonrators of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in September. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

*An Agricultural Course* of instruction, extending over two years, is now organised under the general direction of Mr. M. J. R. Dunstan, M.A., F.R.S.E. It includes instruction in chemistry, botany, agriculture, with practical work on experimental fields, dairy work, farriery, land surveying, &c. The instruction is designed for those who intend to become farmers, bailiffs, land agents, or colonists, and may be extended to a third year if desired. Fee, £15 per annum for residents in Notts, £20 to residents in other counties.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

## FIRTH COLLEGE, SHEFFIELD.

*Professor of Chemistry*—W. Carleton Williams, B.Sc., F.C.S.
*Demonstrators and Assistant Lecturers* — G. Young, Ph.D., and L. T. O'Shea, B.Sc., F.C.S.,

The Session will commence on October 7th.

*First Coures.*—Chemistry of the Non-Metallic Elements. Tuesday and Friday from 10 to 11 a.m. Fee, £2 12s. 6d.

*Second Course.*—Chemistry of Metals. Monday and Thursday from 10 to 11 a.m. £2 12s. 6d.

*Third Course.*—Inorganic Chemistry, Honours Course, Monday, 3. Fee, £1 11s. 6d.

*Fourth Course.*—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 12s. 6d. Chemical Philosophy, Thursday, 11 to 12. Fee, £1 11s. 6d.

*Fifth Course.*—Organic Chemistry, Honours Course, Thursday, 4. Fee, £1 11s. 6d.

Short Courses of Lectures are also given by L. T. O'Shea on Electrolytic Analysis, the Chemistry of Coal Mining, and on Thermic Chemistry.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

*Laboratory.*—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Students who have worked for three sessions in the

Chemical Laboratory are eligible for election to a scholarship value £150 for two years.

*Evening Classes.*—Lectures, Wednesday, 8 to 9. Laboratory instruction, Wednesday, 6 to 9, and another series to be arranged if desired. Sessional Fee, one evening per week, £1 10s.; two, 50s.; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

## UNIVERSITY COLLEGE, DUNDEE.

*Professor of Chemistry*—James Walker, Ph.D., D.Sc.

*Assistant Lecturers*—F. J. Hambly, F.I.C., and J. R. Appleyard, F.C.S.

*Lecture Assistant and Laboratory Steward*—J. Foggie, F.C.S.

The Winter Session begins on October 12th, and ends in March. The Summer Session extends from the middle of April to the end of June.

*The First Year's Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

*Advanced Courses*, of about fifty lectures each, will be given during the year as follows :—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. To supplement the Practical work of First Year's Laboratory Students a short course of Lectures on *Analytical Chemistry* will be offered. Special facilities are afforded to Research Students.

The Lectures and Laboratory Practice in Chemistry are recognised by the Medical Colleges of London and Edinburgh, as well as by the Universities of Edinburgh and Glasgow, for degrees in Science and Medicine. The Courses are suitable for the degrees of the University of London and for the Civil Service appointments, and will also satisfy the requirements of Students in Pharmacy, and of Students who intend to become candidates for the Associateship of the Institute of Chemistry, as far as qualification in Chemistry is concerned.

## UNIVERSITY OF EDINBURGH.

### DEPARTMENT OF CHEMISTRY.

*Professor*—Alex. Crum Brown, M.D., D.Sc., F.R.S., Pres. C.S.

*Lecturers*—L. Dobbin, Ph.D., and H. Marshall, D.Sc.

*Assistant*—W. W. Taylor, M.A.

The working terms are—Winter Session, from middle of October to middle of March ; Summer Session, from beginning of May to end of July.

*Lecture Courses.*—During the Winter Session a General Course of Chemistry for medical and science students is given by the Professor. The class meets daily ; fee £4 4s. An Advanced Course of twenty-five lectures is also given in the Winter Session ; fee, £2 2s. A class on Organic Chemistry is held in summer ; fee, £2 2s. There is also a class on Chemical Theory, by Dr. Dobbin ; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall ; fee, £2 2s. All these Lectures, except the General Course, are now open to women.

In addition to the above, Lecture Courses are given by the Assistants on some particular branch of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Tutorial classes are held in connection with the General Course.

*Laboratories.*—Practical classes for Medical Students meet daily during the latter part of the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s., Oct.-Dec., Jan.-March ; or Summer Session, £5 5s. Half Day—Winter Session, £6 6s., Oct.-Dec., Jan.-March ; or Summer Session, £3 3s. Preference will be given to students in the above order. Students who are not Matriculated may attend the Chemical Laboratory on payment of the entrance fee of 5s. in addition to the Laboratory fees. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

*Graduation.*—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English ; (2) Latin, Greek, French, or German ; (3) Mathematics ; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical languages, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Second B.Sc. Examination includes any three or more of the following subjects :—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy, including Anthropology, Physiology, Geology, including Mineralogy, Zoology, including Comparative Anatomy, and Botany, including Vegetable Physiology. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry ; Organic Chemistry ; Physical Chemistry ; Chemical Crystallography ; History of Chemistry. Practical Examination :—Complex Qualitative Analysis ; Quantitative Analysis, including Gas Analysis and Organic Analysis ; Preparation of Pure Substances, organic and inorganic ; Physico-chemical Measurements.

In the Courses for Final Examination in Pure Science, two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed ; the same regulations apply also to the Practical and Oral Examinations.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches :—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy ; (2) Organic Chemistry ; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

## HERIOT-WATT COLLEGE, EDINBURGH.

*Professor*—John Gibson, Ph.D., F.R.S.E.

*Assistant Professor*—John E. Mackenzie, Ph.D., B.Sc.

*Demonstrators*—Andrew F. King and James B. Shand.

The Session begins October 6th, 1896.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Lecture Course to day students in Chemistry is mainly devoted to Inorganic Chemistry. In the Laboratory course each student is required to prepare and study the properties of the principal elementary and compound gases ; to perform the more important experiments shown by the Professor in the Lecture Room ; to make himself thoroughly acquainted with the preparation and purifica-

tion of a number of salts. After a careful study of the reactions of the principal metals and acids, he passes on to a full course of systematic qualitative analysis, and may then, if attending a second year, take up an extensive course of quantitative analysis (gravimetric, volumetric, and electrolytic), ultimately making a speciality of any branch of the subject which may be most necessary for his future work. Great attention has been paid to the thorough equipment of the Advanced Laboratories, and special facilities are given to advanced students who may wish to engage in any class of Research (Inorganic or Organic) whether of a purely chemical or of a technical nature.

The teaching in the Evening Classes is based on the Syllabus of the Science and Art Department, and includes Elementary, Advanced, and Honours Courses in Theoretical and Practical Inorganic and Organic Chemistry.

## GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

*Professor of Chemistry*—G. G. Henderson, D.Sc., M.A.
*Professor of Technical Chemistry*—E. J. Mills, D.Sc., F.R.S.
*Professor of Metallurgy*—A. Humboldt Sexton, F.C.S., F.R.S.E.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

Complete courses of instruction in Metallurgy and Mining will be given in both Day and Evening Classes.

Copies of the Calendar for 1896-97 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

## UNIVERSITY OF ST. ANDREWS.
### UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

*Professor of Chemistry* — T. Purdie, B.Sc., Ph.D., F.R.S.

The Session begins on October 7th. A Competitive Examination, open to intending Students of Arts or Science, for about fifty Entrance Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 26th and following days. About twenty of these Bursaries are restricted to Men and thirty to Women, twenty of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. Two are open to students of either sex. Two Scholarships of £100 each, tenable for one year, will be open for competition to Graduates of Science at the close of Session 1895-96. A Hall of Residence is provided for Women Students. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

*Lecture Courses.*

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

*First Year's Course.*—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily ; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment. The Lectures are supplemented by a short Course of Laboratory Practice, intended to illustrate the principles of the science.

These courses of instruction are intended to meet the requirements of the Arts' Curriculum; also of candidates for the First B.Sc. Examination, and of students of medicine, so far as Theoretical Chemistry is concerned.

*Second Year's Course.*—The first part of the Course is devoted to Organic Chemistry, and the second part treats of the General Principles and Theory of Chemistry; and of more advanced Inorganic Chemistry, the instruction in general being such as is required for the Second B.Sc. Examination.

Certificates are awarded on the results of examinations, and the " Forrester Prize " of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £3 3s.

*Practical Chemistry.*

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises :— (1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry ; (2) Qualitative and Quantitative Analysis ; (3) Original Investigation. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the First and Second B.Sc. Examinations, and for Students of Medicine.

The fees for Practical Chemistry vary according to the number of hours taken weekly. A certain number of working places in the Laboratory will be available without fee for students who are capable of undertaking original investigation.

## QUEEN'S COLLEGE, BELFAST.

*Professor.*—E. A. Letts, Ph.D., D.Sc., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on three days of each week after May 1st, at 2 p.m. The course is divided into three parts :—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

*Scholarships.*—In addition to various Scholarships awarded in the Faculties of Arts and Medicine in which Chemistry forms a part of the examination, there are other valuable Scholarships awarded specially in connection with the schools of Chemistry and Physics.

## QUEEN'S COLLEGE, CORK.

*Professor*—Augustus E. Dixon, M.D.
*Demonstrator*—R. E. Doran, F.C.S.

The College Session begins on October 20th, 1896, and ends on June 12th, 1897. The classes are open to male and female students.

*Systematic Chemistry.*—(1) General course of Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.—Fee for each Sessional Course, £2. Each subsequent Course, £1. (2) Advanced Organic Chemistry, and Chemical Philosophy.

*Practical Chemistry.*—(1) The General Course of Practical Chemistry, consisting of about forty Lectures, begins on January 4th, 1897. Fee for each Sessional Course, £3. (2) It is contemplated to also hold a Summer Course of Practical Chemistry, commencing in March. Students desiring to attend this Course must send their names to the Registrar on or before the 30th November, 1896, in order to allow the final arrangements to be published before Christmas. (3) A Course for Pharmaceutical Students. (4) Special Courses.

The Chemical Laboratory is open daily from 10 to 4 o'clock (except during class hours and on Saturdays) under the Superintendence of the Professor, to Students entering for special courses of qualitative and quantitative analysis; organic chemistry; or for the purpose of original investigation.

## QUEEN'S COLLEGE, GALWAY.

*Professor*—Alfred Senier, Ph.D., M.D., F.I.C.
*Demonstrator*—A. J. Walker, B.A.

The College Session is divided into three terms. The First Term extends from October 20 to December 23, the Second Term from January 7 to April 10, and the Third Term from April 26 to June 12.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

*Lecture Courses. Faculty of Arts.* — 1. Second year's Course, Inorganic and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—1. First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—1. First year's Course, Inorganic Chemistry.

*Laboratory Courses. Faculty of Arts.* — 1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.* — 1. Second year's Course, Inorganic and Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

For Fees and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

## ROYAL COLLEGE OF SCIENCE FOR IRELAND,
### STEPHEN'S GREEN, DUBLIN.
#### (SCIENCE AND ART DEPARTMENT).

*Professor of Chemistry*—W. N. Hartley, F.R.S.
*Assistant Chemist*—Hugh Ramage, F.I.C., Associate of the Royal College of Science, Dublin.
*Demonstrator of Chemistry and Assaying* — J. Holms Pollok, B.Sc.

The Session commences on Tuesday, October 6th, 1896.

The Royal College of Science for Ireland supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Mining, Engineering, and Manufactures, Physics, and Natural Science. The Diploma of Associate of the Royal College of Science in the Faculty of Manufactures is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as ualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Advanced Chemistry, including Chemical Manufactures and Metallurgy; (3) Analytical and Experimental Chemistry; (4) Instructions in Chemical Research.

Fees payable by Non-Associates :—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£2 for a special course of one month; £5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months £12 for the entire session.

NOTE.—Important changes have been made in the Curriculum for Associate Students. Full particulars are contained in the Directory of the College, which may be had on application to the Secretary.

The following are supplementary courses of instruction arranged for those who are attending a Course of Lectures :—

(1) Laboratory Instruction in the Theory of Chemistry. (2) An Analytical Course for Students in Engineering. (3) A Course of Practical Chemistry for Medical Students. (4) The Analysis of Water, Air, Food, and Drugs, intended for the instruction of Public Analysts and Medical Officers of Health. (5) Assaying.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Examinations of the Department of Science and Art.

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# CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches : the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. Programme, with Syllabus of Subjects, &c., may be obtained of Messrs. Whittaker and Co., Paternoster Square, London, or through any bookseller, price 10d., net. — *City and Guilds Technical College, Exhibition Road.*— Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manu-

factures or Arts. The main purpose of the instruction given is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations will begin on Monday, Sept. 21st, and the Winter Session opens on Tuesday, October

*City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receivy supplementary instruction in the application of Sciencd and of Art to the trades and manufactures in which thes, are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College at 10 o'clock on Tuesday, September 22nd, 1896. *South London Technical Art School.*—Classes in Modelling, Design, Wood Engraving, Drawing and Painting, House Decoration, Machine Drawing and Design, Plaster-work, &c.

CITY OF LONDON COLLEGE, White Street. Moorfields. —Courses of Evening Lectures and Laboratory Practice in Chemistry and Physics, conducted by Mr. I. S. Scarf, F.I.C., F.C.S., assisted by Messrs. J. Davis, H. V. Buttfield, F.C.S., and C. A. West. Session commences Oct. 1.

BATTERSEA POLYTECHNIC.—Principal, Mr. Sidney H. Wells. Wh. Sc. Inorganic, Organic, and Technological Chemistry, Mr. W. A. Bone, M.Sc. (Vict.), Ph.D,, assisted by Mr. J. Wilson, B.Sc. (Vict.). Day and Evening Classes in Science and Art subjects.

BIRKBECK LITERARY AND SCIENTIFIC INSTITUTION, BREAM'S BUILDINGS, CHANCERY LANE. — Chemistry Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. J. Woodward, B.A., B.Sc. Lectures — Elementary, Tuesdays, 8.15 p.m.; Advanced, Thursdays, 6.15; Practical, Tuesdays, 6—9 p.m.; Thursdays, 7.30—9.30 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 6 to 7 p.m.; Practical, Wednesdays, 7 to 9 p.m.

THE CENTRAL SCHOOL OF CHEMISTRY AND PHARMACY. 173, Marylebone Road, London.— Dr. A. B. Griffiths, F.R.S.E., F.C.S., &c., and Mr. Lionel Cooper, F.C.S. Lectures are given on Chemistry, Physics, Botany, Materia Medica, Pharmacy, &c. Laboratory Instruction.

SOUTH LONDON SCHOOL OF PHARMACY, Lim., 325, Kennington Road, S.E.—Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 12 noon. Lectures on Botany daily at 1 p.m. and at 2.30 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S. The Students' Laboratory of this Institution is specially designed to accommodate 40

Students. The Technical Laboratory is open daily from 9 till 5, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months 12 guineas; afterwards 3 guineas per month respectively, inclusive of all departments.

SOUTH-WEST LONDON POLYTECHNIC, Mauresa Road, Chelsea.—Principal, Herbert Tomlinson, B.A., F.R.S. Technical Day Classes in Chemical Industries, commencing September 29th.

THE GOLDSMITHS' INSTITUTE, New Cross, S.E.—Head of the Chemistry Department, Mr. A. G. Bloxam, F.I.C.; Assistants, Mr. H. C. L. Bloxam, and others. Lectures and Practical Classes in General Chemistry, also in Chemistry applied to Gas Manufacture and other industries, are held in the evenings from 7.30 to 10.0, and are open to both sexes. Special attention is paid to Technical Laboratory work and the investigation of manufacturing difficulties.

PEOPLE'S PALACE, Mile End Road, E. (Draper's Company's Institute).—Professor, J. T. Hewitt, M.A., D.Sc., Ph.D.; Assistant, Mr. F. G. Pope. The classes are open to both sexes without limit of age. Evening classes in Theoretical and Practical Chemistry. The Session commences on Monday, September 21st. A Course for the London University B.Sc. Degree, including Honours, is now offered, and the Chemical Laboratory has been newly equipped. Every facility is offered to Students desiring to undertake Research work.

POLYTECHNIC INSTITUTE, 309, Regent Street, London, W.—Mr. R. A. Ward and Assistants.—Evening Classes in Theoretical and Practical Chemistry, &c.. The Classes are open to both sexes. The next term commences on Monday, September 28th.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C. (Science Department of the Univ. Corr. Coll.).—The large Chemical, Biological, and Physical laboratories have been found admirably suited to their purpose, and the proportion of passes in the London University Science Lists has increased rapidly. Students may work either for long or short periods, either for examination or for private practice. The Laboratories accommodate over 100 Students.

WESTMINSTER COLLEGE OF CHEMISTRY AND PHARMACY, Trinity Square, Borough, S.E. — Messrs. Wills and Wootton. Day and Evening Classes.

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THE CLIFTON LABORATORY, Berkeley Square, Bristol.— Principal, E. H. Cook, D.Sc. (Lond.), F.I.C. Students are received either as Private Pupils or Members of a Class. Instruction is given to those requiring to use science or scientific methods in Commercial and Industrial pursuits, or in preparing for Examinations. Students are urged to undertake researches and receive special attention from the teachers. Every effort is made to produce thorough chemists rather than successful examinees.

LEEDS SCHOOL OF SCIENCE AND TECHNOLOGY, (Mechanics' Institution, Leeds).—Lecturer on Chemistry, Mr. S. J. Harris, M.Sc. Assistant Lecturer, Mr. R. W. Ferguson, A.R.C.S. Lecturer on Metallurgy, Mr. B. A. Burrell, F.I.C. Lecturer on Physics, Mr. J. E. Tindall, B.Sc. The Chemical Laboratory is open for four evenings, and the Metallurgical Laboratory for two evenings per week. There is a three years' course of lectures in Inorganic Chemistry, and a two years' course in Organic Chemistry and Metallurgy. The laboratory courses in Physics and Chemistry prepare for the final B.Sc. examination at London University.

INSTITUTE OF CHEMICAL TECHNOLOGY, Hackins Hey, Liverpool (A. Norman Tate and Co.).—Principal, Mr. F. H. Tate, F.C.S. The course of instruction is intended

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TECHNICAL INSTITUTE, Birley Street, Beswick.— Demonstrator in Chemistry, Mr. R. J. B. Sanderson.

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ABERDEEN UNIVERSITY.—Prof. Japp.

SCHOOL OF MEDICINE, Edinburgh.—Dr. S. Macadam, Mr. King, Mr. I. Macadam, and Drs. Aitken and Readman.

ST. MUNGO'S COLLEGE AND SCHOOL OF MEDICINE, EDINBURGH.—Dr. Marshall.

SURGEON'S HALL, Nicolson Street, Edinburgh.—Mr. Ivison Macadam. Laboratory work and demonstrations in Agricultural Chemistry. Chemistry Class for Women.

GLASGOW UNIVERSITY.—Prof. J. Ferguson.

GLASGOW VETERINARY COLLEGE.—Professor, T. L. Goodwin, Systematic Course, Oct. 6 to May 9. Laboratory daily, except Saturdays, for private students. Saturday class for teachers, 9 to 1.

ANDERSON'S COLLEGE, GLASGOW.—Mr. J. R. Watson.

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ROYAL COLLEGE OF SURGEONS IN IRELAND, DUBLIN.— Professor of Chemistry and Hygiene: Sir Charles A. Cameron, M.D., F.R.C.S.I. Instruction is given in the College Laboratory in General, Practical, and Analytical Chemistry, and in the subjects (Physical, Chemical, and Microscopical) required for Examinations in Public Health and to educate for the position of Public Analyst.

DUBLIN, CATHOLIC UNIVERSITY.—Dr. Campbell.

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LIVERPOOL, 1896.

INAUGURAL ADDRESS OF THE PRESIDENT,
SIR JOSEPH LISTER, BART., D.C.L., LL.D., F.R.S.

MY Lord Mayor, my Lords, Ladies, and Gentlemen, I have first to express my deep sense of gratitude for the great honour conferred upon me by my election to the high office which I occupy to-day. It came upon me as a great surprise. The engrossing claims of surgery have prevented me for many years from attending the meetings of the Association, which excludes from her sections medicine in all its branches. This severance of the art of healing from the work of the Association was right and indeed inevitable. Not that medicine has little in common with science. The surgeon never performs an operation without the aid of anatomy and physiology; and in what is often the most difficult part of his duty, the selection of the right course to follow, he, like the physician, is guided by pathology, the science of the nature of disease, which, though very difficult from the complexity of its subject matter, has made during the last half-century astonishing progress; so that the practice of medicine in every deparment is becoming more and more based on science as distinguished from empiricism. I propose on the present occasion to bring before you some illustrations of the interdependence of science and the healing art; and the first that I will take is perhaps the most astonishing of all results of purely physical inquiry —the discovery of the Röntgen rays, so called after the man who first clearly revealed them to the world. Mysterious as they still are, there is one of their properties which we can all appreciate—their power of passing through substances opaque to ordinary light. There seems to be no relation whatever between transparency in the common sense of the term and penetrability to these emanations. The glasses of a pair of spectacles may arrest them, while their wooden and leathern case allows them to pass almost unchecked. Yet they produce, whether directly or indirectly, the same effects as light upon a photographic plate. As a general rule the denser any object is the greater obstacle does it oppose to the rays. Hence, as bone is denser than flesh, if the hand or other part of the body is placed above the sensitive film enclosed in a case of wood or other light material at a suitable distance from the source of the rays, while they pass with the utmost facility through the uncovered parts of the lid of the box and powerfully affect the plate beneath, they are arrested to a large extent by the bones, so that the plate is little acted upon in the parts opposite to them, while the portions corresponding to the muscles and other soft parts are influenced in an intermediate degree. Thus a picture is obtained in which the bones stand out in sharp relief among the flesh, and anything abnormal in their shape or position is clearly displayed.

I need hardly point out what important aid this must give to the surgeon. As an instance, I may mention a case which occurred in the practice of Mr. Howard Marsh. He was called to see a severe injury of the elbow, in which the swelling was so great as to make it impossible for him by ordinary means of examination to decide whether he had to deal with a fracture or a disloca-

tion. If it were the latter, a cure would be effected by the exercise of violence, which would be not only useless but most injurious if a bone was broken. By the aid of the Röntgen rays a photograph was taken, in which the bone of the upper arm was clearly seen displaced forwards on those of the forearm. The diagnosis being thus established, Mr. Marsh proceeded to reduce the dislocation; and his success was proved by another photograph which showed the bones in their natural relative position.

The common metals, such as lead, iron, and copper, being still denser than the osseous structures, these rays can show a bullet embedded in a bone or a needle lodged about a joint. At the last conversazione of the Royal Society, a picture produced by the new photography displayed with perfect distinctness through the bony framework of the chest a halfpenny low down in a boy's gullet. It had been there for six months, causing uneasiness at the pit of the stomach during swallowing; but whether the coin really remained impacted, or if so, what was its position, was entirely uncertain till the Röntgen rays revealed it. Dr. Macintyre, of Glasgow, who was the photographer, informs me that when the presence of the halfpenny had been thus demonstrated, the surgeon in charge of the case made an attempt to extract it, and, although this was not successful in its immediate object, it had the effect of dislodging the coin, for a subsequent photograph by Dr. Macintyre not only showed that it had disappeared from the gullet, but also, thanks to the wonderful penetrating power which the rays had acquired in his hands, proved that it had not lodged further down in the alimentary passage. The boy has since completely recovered.

The Röntgen rays cause certain chemical compounds to fluoresce, and emit a faint light plainly visible in the dark; and if they are made to fall upon a translucent screen impregnated with such a salt, it becomes beautifully illuminated. If a part of the human body is interposed between the screen and the source of the rays, the bones and other structures are thrown in shadow upon it, and thus a diagnosis can be made without the delay involved in taking a photograph. It was in fact in this way that Dr. Macintyre first detected the coin in the boy's gullet. Mr. Herbert Jackson, of King's College, London, early distinguished himself in this branch of the subject. There is no reason to suppose that the limits of the capabilities of the rays in this way have yet been reached. By virtue of the greater density of the heart than the adjacent lungs with their contained air, the form and dimensions of that organ in the living body may be displayed on the fluorescent screen, and even its movements have been lately seen by several different observers.

Such important applications of the new rays to medical practice have strongly attracted the interest of the public to them, and I venture to think that thay have even served to stimulate the investigations of physicists. The eminent Professor of Physics in the University College of this city (Professor Lodge) was one of the first to make such practical applications, and I was able to show to the Royal Society at a very early period a photograph, which he had the kindness to send me, of a bullet embedded in the hand. His interest in the medical aspect of the subject remains unabated, and at the same time he has been one of the most distinguished investigators of its purely physical side.

There is another way in which the Röntgen rays connect themselves with physiology, and may possibly influence medicine. It is found that if the skin is long exposed to their action it becomes very much irritated, affected with a sort of aggravated sun-burning. This suggests the idea that the transmission of the rays through the human body may be not altogether a matter of indifference to internal organs, but may, by long-continued action, produce, according to the condition of the part concerned, injurious irritation or salutary stimulation.

This is the jubilee of Anæsthesia in surgery. That priceless blessing to mankind came from America. It had, indeed, been foreshadowed in the first year of this century by Sir Humphry Davy, who, having found a toothache from which he was suffering relieved as he inhaled laughing gas (nitrous oxide), threw out the suggestion that it might perhaps be used for preventing pain in surgical operations. But it was not till, on September 30, 1846, Dr. W. T. G. Morton, of Boston, after a series of experiments upon himself and the lower animals, extracted a tooth painlessly from a patient whom he had caused to inhale the vapour of sulphuric ether, that the idea was fully realised. He soon afterwards publicly exhibited his method at the Massachusetts General Hospital, and after that event the great discovery spread rapidly over the civilised world. I witnessed the first operation in England under ether. It was performed by Robert Liston in University College Hospital, and it was a complete success. Soon afterwards I saw the same great surgeon amputate the thigh as painlessly, with less complicated anæsthetic apparatus, by aid of another agent, chloroform, which was being powerfully advocated as a substitute for ether by Dr. (afterwards Sir James Y.) Simpson, who also had the great merit of showing that confinements could be conducted painlessly, yet safely, under its influence. These two agents still hold the field as general anæsthetics for protracted operations, although the gas originally suggested by Davy, in consequence of its rapid action and other advantages, has taken their place in short operations, such as tooth extraction. In the birthplace of anæsthesia ether has always maintained its ground; but in Europe it was to a large extent displaced by chloroform till recently, when many have returned to ether, under the idea that, though less convenient, it is safer. For my own part, I believe that chloroform, if carefully administered on right principles, is, on the average, the safer agent of the two.

The discovery of anæsthesia inaugurated a new era in surgery. Not only was the pain of operations abolished, but the serious and sometimes mortal shock which they occasioned to the system was averted, while the patient was saved the terrible ordeal of preparing to endure them. At the same time the field of surgery became widely extended, since many procedures in themselves desirable, but before impossible from the protracted agony they would occasion, became matters of routine practice. Nor have I by any means exhausted the list of the benefits conferred by this discovery.

Anæsthesia in surgery has been from first to last a gift of science. Nitrous oxide, sulphuric ether, and chloroform are all artificial products of chemistry, their employment as anæsthetics was the result of scientific investigation, and their administration, far from being, like the giving of a dose of medicine, a matter of rule-of-thumb, imperatively demands the vigilant exercise of physiological and pathological knowledge.

While rendering such signal service to surgery, anæsthetics have thrown light upon biology generally. It has been found that they exert their soporific influence not only upon Vertebrata, but upon animals so remote in structure from man as bees and other insects. Even the functions of vegetables are suspended by their agency. They thus afford strong confirmation of the great generalisation that living matter is of the same essential nature wherever it is met with on this planet, whether in the animal or vegetable kingdom. Anæsthetics have also, in ways to which I need not here refer, powerfully promoted the progress of physiology and pathology.

My next illustration may be taken from the work of Pasteur on fermentation. The prevailing opinion regarding this class of phenomena when they first engaged his attention was that they were occasioned primarily by the oxygen of the air acting upon unstable animal or vegetable products, which, breaking up under its influence, communicated disturbance to other organic materials in their vicinity, and thus led to their decomposition,

Cagniard-Latour had indeed shown several years before that yeast consists essentially of the cells of a microscopic fungus which grows as the sweetwort ferments; and he had attributed the breaking up of the sugar into alcohol and carbonic acid to the growth of the microorganism. In Germany, Schwann, who independently discovered the yeast plant, had published very striking experiments in support of analogous ideas regarding the putrefaction of meat. Such views had also found other advocates, but they had become utterly discredited, largely through the great authority of Liebig, who bitterly opposed them.

Pasteur, having been appointed as a young man Dean of the Faculty of Sciences in the University of Lille, a town where the products of alcoholic fermentation were staple articles of manufacture, determined to study that process thoroughly; and as a result he became firmly convinced of the correctness of Cagniard-Latour's views regarding it. In the case of other fermentations, however, nothing fairly comparable to the formation of yeast had till then been observed. This was now done by Pasteur for that fermentation in which sugar is resolved into lactic acid. This lactic fermentation was at that time brought about by adding some animal substance, such as fibrin, to a solution of sugar, together with chalk, that should combine with the acid as it was formed. Pasteur saw, what had never before been noticed, that a fine grey deposit was formed, differing little in appearance from the decomposing fibrin, but steadily increasing as the fermentation proceeded. Struck by the analogy presented by the increasing deposit to the growth of yeast in sweetwort, he examined it with the microscope, and found it to consist of minute particles of uniform size. Pasteur was not a biologist, but although these particles were of extreme minuteness in comparison with the constituents of the yeast plant, he felt convinced that they were of an analogous nature, the cells of a tiny microscopic fungus. This he regarded as the essential ferment, the fibrin or other so-called ferment serving, as he believed, merely the purpose of supplying to the growing plant certain chemical ingredients not contained in the sugar, but essential to its nutrition. And the correctness of this view he confirmed in a very striking manner, by doing away with the fibrin or other animal material altogether, and substituting for it mineral salts containing the requisite chemical elements. A trace of the grey deposit being applied to a solution of sugar containing these salts in addition to the chalk, a brisker lactic fermentation ensued than could be procured in the ordinary way.

I have referred to this research in some detail because it illustrates Pasteur's acuteness as an observer and his ingenuity in experiment, as well as his almost intuitive perception of truth.

A series of other beautiful investigations followed, clearly proving that all true fermentations, including putrefaction, are caused by the growth of micro-organisms.

It was natural that Pasteur should desire to know how the microbes, which he showed to be the essential causes of the various fermentations, took their origin. It was at that period a prevalent notion, even among many eminent naturalists, that such humble and minute beings originated *de novo* in decomposing organic substances; the doctrine of spontaneous generation, which had been chased successively from various positions which it once occupied among creatures visible to the naked eye, having taken its last refuge where the objects of study were of such minuteness that their habits and history were correspondingly difficult to trace. Here again Pasteur at once saw, as if by instinct, on which side the truth lay; and, perceiving its immense importance, he threw himself with ardour into its demonstration. I may describe briefly one class of experiments which he performed with this object. He charged a series of narrow-necked glass flasks with a decoction of yeast, a liquid peculiarly liable to alteration on exposure to the air. Having boiled the liquid in each

flask, to kill any living germs it might contain, he sealed its neck with a blowpipe during ebullition; after which, the flask being allowed to cool, the steam within it condensed, leaving a vacuum above the liquid. If, then, the neck of the flask were broken in any locality, the air at that particular place would rush in to fill the vacuum, carrying with it any living microbes that might be floating in it. The neck of the flask having been again sealed, any germs so introduced would in due time manifest their presence by developing in the clear liquid. When any of such a series of flasks were opened and re-sealed in an inhabited room, or under the trees of a forest, multitudes of minute living forms made their appearance in them; but if this was done in a cellar long unused, where the suspended organisms, like other dust, might be expected to have all fallen to the ground, the decoction remained perfectly clear and unaltered. The oxygen and other gaseous constituents of the atmosphere were thus shown to be of themselves incapable of inducing any organic development in yeast-water.

Such is a sample of the many well-devised experiments by which he carried to most minds the conviction that, as he expressed it, "*la génération spontanée est une chimère,*" and that the humblest and minutest living organisms can only originate by parentage from beings like themselves.

Pasteur pointed out the enormous importance of these humble organisms in the economy of Nature. It is by their agency that the dead bodies of plants and animals are resolved into simpler compounds fitted for assimilation by new living forms. Without their aid the world would be, as Pasteur expresses it, *encombré de cadavres.* They are essential not only to our well-being, but to our very existence. Similar microbes must have discharged the same necessary function of removing refuse and providing food for successive generations of plants and animals during the past periods of the world's history; and it is interesting to think that organisms as simple as can well be conceived to have existed when life first appeared upon our globe have, in all probability, propagated the same lowly but most useful offspring during the ages of geological time.

Pasteur's labours on fermentation have had a very important influence upon surgery. I have been often asked to speak on my share in this matter before a public audience; but I have hitherto refused to do so, partly because the details are so entirely technical, but chiefly because I have felt an invincible repugnance to what might seem to savour of self-advertisement. The latter objection now no longer exists, since advancing years have indicated that it is right for me to leave to younger men the practice of my dearly loved profession. And it will perhaps be expected that, if I can make myself intelligible, I should say something upon the subject on the present occasion.

Nothing was formerly more striking in surgical experience than the difference in the behaviour of injuries according to whether the skin was implicated or not. Thus, if the bones of the leg were broken and the skin remained intact, the surgeon applied the necessary apparatus without any other anxiety than that of maintaining a good position of the fragments, although the internal injury to bones and soft parts might be very severe. If, on the other hand, a wound of the skin was present communicating with the broken bones, although the damage might be in other respects comparatively slight, the compound fracture, as it was termed, was one of the most dangerous accidents that could happen. Mr. Syme, who was, I believe, the safest surgeon of his time, once told me that he was inclined to think that it would be, on the whole, better if all compound fractures of the leg were subjected to amputation, without any attempt to save the limb. What was the cause of this astonishing difference? It was clearly in some way due to the exposure of the injured parts to the external world. One obvious effect of such exposure was indicated by the odour of the discharge, which showed that the blood in the wound had undergone putrefactive change by which the bland nutrient liquid had been converted into highly irritating and poisonous substances. I have seen a man with compound fracture of the leg die within two days of the accident, as plainly poisoned by the products of putrefaction as if he had taken a fatal dose of some potent toxic drug.

An external wound of the soft parts might be healed in one of two ways. If its surfaces were clean cut and could be brought into accurate apposition, it might unite rapidly and painlessly "by the first intention." This, however, was exceptional. Too often the surgeon's efforts to obtain primary union were frustrated; the wound inflamed and the retentive stitches had to be removed, allowing it to gape; and then, as if it had been left open from the first, healing had to be effected in the other way which it is necessary for me briefly to describe. An exposed raw surface became covered in the first instance with a layer of clotted blood or certain of its constituents, which invariably putrefied; and the irritation of the sensitive tissues by the putrid products appeared to me to account sufficiently for the inflammation which always occurred in and around an open wound during the three or four days which elapsed before what were termed "granulations" had been produced. These constituted a coarsely granular coating of very imperfect or embryonic structure, destitute of sensory nerves and prone to throw off matter or pus, rather than absorb, as freshly divided tissues do, the products of putrefaction. The granulations thus formed a beautiful living plaster, which protected the sensitive parts beneath from irritation, and the system generally from poisoning and consequent febrile disturbance. The granulations had other useful properties, of which I may mention their tendency to shrink as they grew, thus gradually reducing the dimensions of the sore. Meanwhile another cause of its diminution was in operation. The cells of the epidermis or scarf-skin of the cutaneous margins were perpetually producing a crop of young cells of similar nature, which gradually spread over the granulations till they covered them entirely, and a complete cicatrix or scar was the result. Such was the other mode of healing, that by granulation and cicatrisation; a process which which, when it proceeded unchecked to its completion, commanded our profound admiration. It was, however, essentially tedious compared with primary union, while, as we have seen, it was always preceded by more or less inflammation and fever, sometimes very serious in their effects. It was also liable to unforeseen interruptions. The sore might become larger instead of smaller, cicatrisation giving place to ulceration in one of its various forms, or even to the frightful destruction of tissue which, from the circumstance that it was most frequently met with in hospitals, was termed hospital gangrene. Other serious and often fatal complications might arise, which the surgeon could only regard as untoward accidents and over which he had no efficient control.

It will be readily understood from the above description that the inflammation which so often frustrated the surgeon's endeavours after primary union was in my opinion essentially due to decomposition of blood within the wound.

These and many other considerations had long impressed me with the greatness of the evil of putrefaction in surgery. I had done my best to mitigate it by scrupulous ordinary cleanliness and the use of various deodorant lotions. But to prevent it altogether appeared hopeless while we believed with Liebig that its primary cause was the atmospheric oxygen which, in accordance with the researches of Graham, could not fail to be perpetually diffused through the porous dressings which were used to absorb the blood discharged from the wound. But when Pasteur had shown that putrefaction was a fermentation caused by the growth of microbes, and that these could not arise *de novo* in the decomposable substance, the problem assumed a more hopeful aspect. If the wound could be treated with some substance which, without doing, too

serious mischief to the human tissues, would kill the microbes already contained in it and prevent the future access of others in the living state, putrefaction might be prevented, however freely the air with its oxygen might enter. I had heard of carbolic acid as having a remarkable deodorising effect upon sewage, and having obtained from my colleague, Dr. Anderson, Professor of Chemistry in the University of Glasgow, a sample which he had of this product, then little more than a chemical curiosity in Scotland, I determined to try it in compound fractures. Applying it undiluted to the wound, with an arrangement for its occasional renewal, I had the joy of seeing these formidable injuries follow the same safe and tranquil course as simple fractures, in which the skin remains unbroken.

At the same time we had the intense interest of observing in open wounds what had previously been hidden from human view, the manner in which subcutaneous injuries are repaired. Of special interest was the process by which portions of tissue killed by the violence of the accident were disposed of, as contrasted with what had till then been invariably witnessed. Dead parts had been always seen to be gradually separated from the living by an inflammatory process and thrown off as sloughs. But when protected by the antiseptic dressing from becoming putrid and therefore irritating, a structure deprived of its life caused no disturbance in its vicinity; and, on the contrary, being of a nutritious nature, it served as pabulum for the growing elements of the neighbouring living structures, and these became in due time entirely substituted for it. Even dead bone was seen to be thus replaced by living osseous tissue.

This suggested the idea of using threads of dead animal tissue for tying blood vessels; and this was realised by means of catgut, which is made from the intestine of the sheep. If deprived of living microbes, and otherwise properly prepared, catgut answers its purpose completely; the knot holding securely, while the ligature around the vessel becomes gradually absorbed and replaced by a ring of living tissue. The threads, instead of being left long as before, could now be cut short, and the tedious process of separation of the ligature, with its attendant serious danger of bleeding, was avoided.

Undiluted carbolic acid is a powerful caustic; and although it might be employed in compound fracture, where some loss of tissue was of little moment in comparison with the tremendous danger to be averted, it was altogether unsuitable for wounds made by the surgeon. It soon appeared, however, that the acid would answer the purpose aimed at, though used in diluted forms devoid of caustic action, and therefore applicable to operative surgery. According to our then existing knowledge, two essential points had to be aimed at: to conduct the operation so that on its completion the wound should contain no living microbes, and to apply a dressing capable of preventing the access of other living organisms till the time should have arrived for changing it.

Carbolic acid lent itself well to both these objects. Our experience with this agent brought out what was, I believe, a new principle in pharmacology—namely, that the energy of action of any substance upon the human tissues depends not only upon the proportion in which it is contained in the material used as a vehicle for its administration, but also upon the degree of tenacity with which it is held by its solvent. Water dissolves carbolic acid sparingly and holds it extremely lightly, leaving it free to act energetically on other things for which it has greater affinity, while various organic substances absorb it greedily and hold it tenaciously. Hence its watery solution seemed admirably suited for a deterrent lotion to be used during the operation for destroying any microbes that might fall upon the wound, and for purifying the surrounding skin and also the surgeon's hands and instruments. For the last-named purpose it had the further advantage that it did not act on steel.

For an external dressing the watery solution was not adapted, as it soon lost the acid it contained, and was irritating while it lasted. For this purpose some organic substances were found to answer well. Large proportions of the acid could be blended with them in so bland a form as to be unirritating; and such mixtures, while perpetually giving off enough of the volatile salt to prevent organic development in the discharges that flowed past them, served as a reliable store of the antiseptic for days together.

The appliances which I first used for carrying out the antiseptic principle were both rude and needlessly complicated. The years that have since passed have witnessed great improvements in both respects. Of the various materials which have been employed by myself and others, and their modes of application, I need say nothing except to express my belief, as a matter of long experience, that carbolic acid, by virtue of its powerful affinity for the epidermis and oily matters associated with it, and also its great penetrating power, is still the best agent at our disposal for purifying the skin around the wound. But I must say a few words regarding a most important simplification of our procedure. Pasteur, as we have seen, had shown that the air of every inhabited room teems with microbes; and for a long time I employed various more or less elaborate precautions against the living atmospheric dust, not doubting that, as all wounds except the few which healed completely by the first intention underwent putrefactive fermentation, the blood must be a peculiarly favourable soil for the growth of putrefactive microbes. But I afterwards learnt that such was by no means the case. I had performed many experiments in confirmation of Pasteur's germ theory, not indeed in order to satisfy myself of its truth, but in the hope of convincing others. I had observed that uncontaminated milk, which would remain unaltered for an indefinite time if protected from dust, was made to teem with microbes of very different kinds by a very brief exposure to the atmosphere, and that the same effect was produced by the addition of a drop of ordinary water. But when I came to experiment with blood drawn with antiseptic precautions into sterilised vessels, I saw to my surprise that it might remain free from microbes in spite of similar access of air or treatment with water. I even found that if very putrid blood was largely diluted with sterilised water, so as to diffuse its microbes widely and wash them of their acrid products, a drop of such dilution added to pure blood might leave it unchanged for days at the temperature of the body, although a trace of the septic liquid undiluted caused intense putrefaction within twenty-four hours. Hence I was led to conclude that it was the grosser forms of septic mischief, rather than microbes in the attenuated condition in which they existed in the atmosphere, that we had to dread in surgical practice. And at the London Medical Congress in 1881, I hinted, when describing the experiments I have alluded to, that it might turn out possible to disregard altogether the atmospheric dust. But greatly as I should have rejoiced at such a simplification of our procedure, if justifiable, I did not then venture to test it in practice. I knew that with the safeguards which we then employed I could ensure the safety of my patients, and I did not dare to imperil it by relaxing them. There is one golden rule for all experiments upon our fellow-men. Let the thing tried be that which, according to our best judgment, is the most likely to promote the welfare of the patient. In other words, Do as you would be done by.

Nine years later, however, at the Berlin Congress in 1890, I was able to bring forward what was, I believe, absolute demonstration of the harmlessness of the atmospheric dust in surgical operations. This conclusion has been justified by subsequent experience; the irritation of the wound by antiseptic irrigation and washing may therefore now be avoided, and nature left quite undisturbed to carry out her best methods of repair, while the surgeon may conduct his operations as simply as in former days, provided always that, deeply impressed with the tremendous importance of his object, and inspiring the

same conviction in all his assistants, he vigilantly maintains from first to last, with a care that, once learnt, becomes instinctive, but for the want of which nothing else can compensate, the use of the simple means which will suffice to exclude from the wound the coarser forms of septic impurity.

Even our earlier and ruder methods of carrying out the antiseptic principle soon produced a wonderful change in my surgical wards in the Glasgow Royal Infirmary, which, from being some of the most unhealthy in the kingdom, became, as I believe I may say without exaggeration, the healthiest in the world; while other wards, separated from mine only by a passage of a few feet broad, where former modes of treatment were for a while continued, retained their former insalubrity. This result, I need hardly remark, was not in any degree due to special skill on my part, but simply to the strenuous endeavour to carry out strictly what seemed to me a principle of supreme importance.

Equally striking changes were afterwards witnessed in other institutions. Of these I may give one example. In the great Allgemeines Krankenhaus of Munich, hospital gangrene had become more and more rife from year to year, till at length the frightful condition was reached that 80 per cent of all wounds became affected by it. It is only just to the memory of Professor von Nussbaum, then the head of that establishment, to say that he had done his utmost to check this frightful scourge; and that the evil was not caused by anything peculiar in his management was shown by the fact that in a private hospital under his care there was no unusual unhealthiness. The larger institution seemed to have become hopelessly infected, and the city authorities were contemplating its demolition and re-construction. Under these circumstances, Professor von Nussbaum despatched his chief assistant, Dr. Lindpaintner, to Edinburgh, where I at that time occupied the chair of clinical surgery, to learn the details of the antiseptic system, as we then practised it. He remained until he had entirely mastered them, and after his return all the cases were on a certain day dressed on our plan. From that day forward not a single case of hospital gangrene occurred in the Krankenhaus. The fearful disease pyæmia likewise disappeared, and erysipelas soon followed its example.

But it was by no means only in removing the unhealthiness of hospitals that the antiseptic system showed its benefits. Inflammation being suppressed, with attendant pain, fever, and wasting discharge, the sufferings of the patient were, of course, immensely lessened; rapid primary union being now the rule, convalescence was correspondingly curtailed; while as regards safety and the essential nature of the mode of repair, it became a matter of indifference whether the wound had clean-cut surfaces which could be closely approximated, or whether the injury inflicted had been such as to cause destruction of tissue. And operations which had been regarded from time immemorial as unjustifiable were adopted with complete safety.

It pleases me to think that there is an ever-increasing number of practitioners throughout the world to whom this will not appear the language of exaggeration. There are cases in which, from the situation of the part concerned or other unusual circumstances, it is impossible to carry out the antiseptic system completely. These, however, are quite exceptional; and even in them much has been done to mitigate the evil which cannot be altogether avoided.

(To be continued).

**Tea Cigarettes.**—According to the *Indian Pharmacologist*, the demand for tea in India and Ceylon has been stimulated by a new demand which has sprung up in America for its use as a substitute for tobacco in the manufacture of cigarettes. Their use is said to be more deleterious than that of opium. Will a society be formed to agitate for the prohibition of the culture of tea?

# THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JÜPTNER von JONSTORFF
(Neuberg, Austria).

(Continued from p. 118).

7. *Errors caused by Differences in the Calculation of the Analyses based on the Atomic Weights.* — During recent years a series of revisions of the values of the atomic weights have been published, but unfortunately they do not in all cases present the desired agreement among themselves. As, in cases where the greatest possible accuracy is required, it appears only natural to employ these revised values in the calculation of the analyses, it may not be superfluous to discuss them in detail.

The oldest of these new determination is that of F. W. Clarke ("Constants of Nature," 1882). This was followed in 1883 by the work on the "Atomic Weights of the Elements," by L. Meyer and K. Seubert, whose statements, like the previous ones of Clarke, have found the widest circulation in technical circles. In 1886, Van der Plaats (*Ann. de Chim. et de Phys.*, Series 6, vol. vii., April) published the results of his new determinations, and, lastly, in 1893, F. W. Clarke (*Journal of the American Chemical Society*, vol. xvi., p. 179; *Chemisches Centralblatt*, 1894, No. I., p. 810) undertook a revision of the values of the atomic weights previously published by him. As the last values have not yet been generally adopted, his older results must here also be taken into account. The atomic weights of the elements of greatest importance in the iron and steel industries, as set forth in the works cited are as follows:—

| Element. | F. W. Clarke. 1882. | L. Meyer and K. Seubert. Atomic weight. | Possible error. | Van der Plaats. Atomic weight. | Possible error. | Clarke. 1893. |
|---|---|---|---|---|---|---|
| Chromium .. | 52·009 | 52·45 | 0·5-1·0 | 52·3 | 0·3 | 52·1 |
| Iron .. .. | 55·913 | 55·88 | 0·1 | 56·0 | 0·05 | 56·0 |
| Magnesium . | 23·959 | 23·94 | 0·5-1·0 | 24·4 | 0·05 | 24·3 |
| Manganese . | 53·906 | 54·80 | 0·5-1·0 | 55·0 | 0·1 | 55·0 |
| Phosphorus . | 30·958 | 30·96 | 0·1 | 30·95 | 0·05 | 31·0 |
| Oxygen .. | 15·9633 | 15·96 | >0·5 | 16·0 | — | 16·0 |
| Sulphur .. | 31·984 | 31·98 | >0·5 | 32·06 | 0·01 | 32·06 |
| Silicon .. | 28·195 | 28·00 | 0·5-1·0 | 28·0 | 0·1 | 28·4 |
| Barium .. | 137·763 | 136·86 | 0·5 | 137·1 | 0·1 | 137·43 |

From this the figures given in table (see next page) are calculated for some of the more important compounds.

If, in the titration of manganese (by the chlorate method), with ferrous ammonium sulphate and permanganate, the manganese value of the permanganate standard is calculated from its iron value, one atom of manganese corresponds with two atoms of iron. The corresponding atomic weights are then as follows:—

| | Iron. | Manganese. |
|---|---|---|
| Clarke, 1882 .. .. .. | 55·913 | 53·906 |
| L. Meyer and K. Seubert.. | 55·88 | 54·8 |
| Van der Plaats.. .. .. | 56·0 | 55·0 |
| Clarke, 1893 .. .. .. | 56·0 | 55·0 |

Thus, one part by weight of iron represents—

| According to— | Parts by weight of Manganese. |
|---|---|
| Clarke, 1882.. .. .. .. | 0·48205 |
| L. Meyer and K. Seubert .. | 0·49033 |
| Van der Plaats .. .. .. | 0·49107 |
| Clarke, 1893.. .. .. .. | 0·49107 |

The maximum difference is—

$$\Delta_{3-1} = 1·87 \text{ per cent.}$$
$$\Delta_{4-2} = 0·15 \text{ per cent.}$$

* Read before the Iron and Steel Institute.

| Compound. | Clarke. 1882. | L. Meyer and K. Seubert. | Van der Plaats. | Clarke, 1893. | Maximum difference, per cent. |
|---|---|---|---|---|---|
| Ferric oxide, $Fe_2O_3$. — $Fe_2$ | 111·826 | 111·76 | 112·0 | 112·0 | |
| $O_3$ | 47·8899 | 47·28 | 48·0 | 48·0 | |
| $Fe_2O_3$ | 159·7159 | 159·64 | 160·0 | 160·0 | |
| 1 pt. by wt. $Fe_2O_3$ = pt. by wt. Fe | 0·70016 | 0·70008 | 0·70000 | 0·7000 | $\Delta_{1-3}=0·02$ $\Delta_{2-4}=0·01$ |
| Barium sulphate $BaSO_4$. — S | 31·984 | 31·98 | 32·06 | 32·06 | |
| $O_4$ | 63·8532 | 63·84 | 64·00 | 64·00 | |
| Ba | 136·763 | 136·86 | 137·10 | 137·43 | |
| $BaSO_4$ | 232·6002 | 232·68 | 233·16 | 233·49 | |
| 1 pt. by wt. $BaSO_4$ = pt. by wt. S | 0·13750 | 0·13744 | 0·13750 | 0·13730 | $\Delta_{1-2}=0·04$ $\Delta_{3-4}=0·14$ |
| 1 pt. by wt. $BaSO_4$ = pt. by wt. Ba | 0·58797 | 0·58819 | 0·58801 | 0·58859 | $\Delta_{2-1}=0·04$ $\Delta_{4-3}=0·10$ |
| Magnesium pyrophosphate, $Mg_2P_2O_7$. — $Mg_2$ | 47·918 | 47·88 | 48·8 | 48·6 | |
| $P_2$ | 61·916 | 61·92 | 61·9 | 62·0 | |
| $O_7$ | 111·7431 | 111·72 | 112·0 | 112·0 | (a) |
| $Mg_2P_2O_7$. | 221·5771 | 221·52 | 222·7 | 222·6 | |
| 1 pt. by wt. $Mg_2P_2O_7$ = pt. by wt. Mg | 0·21626 | 0·21601 | 0·21913 | 0·21833 | $\Delta_{3-2}=1·44$ |
| Chromium oxide, $Cr_2O_3$. — $Cr_2$ | 104·018 | 104·90 | 104·60 | 104·2 | |
| $O_3$ | 47·8899 | 47·88 | 48·00 | 48·0 | (b) |
| $Cr_2O_3$. | 151·9079 | 152·78 | 152·60 | 152·2 | |
| 1 pt. by wt. $Cr_2O_3$ = pt. by wt. Cr | 0·68474 | 0·68661 | 0·68545 | 0·68462 | $\Delta_{2-4}=0·31$ |
| Silica, $SiO_2$. — Si | 28·195 | 28·0 | 28·0 | 28·4 | |
| $O_2$ | 31·9266 | 31·92 | 32·0 | 32·0 | (c) |
| $SiO_2$. | 60·1216 | 59·92 | 60·0 | 60·4 | |
| 1 pt. by wt. $SiO_2$ = pt. by wt. Si | 0·46897 | 0·46729 | 0·46667 | 0·47019 | $\Delta_{4-3}=0·73$ |

(a) This difference is 0·4 per cent with pure magnesite, with burnt magnesite it amounts to 1·12 per cent.
(b) Difference with a 50 per cent ferrochrome = 0·15 per cent.
(c) Difference with a 14 per cent ferro-silicon = 0·10 per cent, but with pure quartz = 0·73 per cent.

or, with an 80 per cent ferromanganese, 1·5 or 0·12 per cent.

The atomic weights cited above demand attention, however, from another point of view. For example, L. Meyer and K. Seubert give the possible error in the atomic weights of chromium, magnesium, and silicon as 0·5 to 1·0; this means that analyses, in respect of these elements, may possibly be incorrect to the extent of 50/52 to 100/52, 50/24 to 100/24, and 50/28 to 100/28, or about 1 to 2 per cent, 2 to 4 per cent, and 1½ to 3 per cent respectively. It is evident, therefore, that a thorough revision of the atomic weights in question is urgently needed.

(To be continued).

## AN IMPROVED METHOD FOR THE MANUFACTURE OF PEROXIDE OF LEAD.

By H. N. WARREN, Principal Liverpool Research Laboratory.

VARIOUS methods have been devised for the preparation of the above compound, which is now largely consumed in commercial quarters. But hitherto each process presents drawbacks either in one direction or the other. An analytical method of long standing, namely, the action that nitric acid affords when brought into contact with the red lead of commerce, yields a pure oxide, yet at the same time, besides being costly, it also produces by-products. Again, on the other hand, the use of alkaline hypochlorites produces an oxide contaminated more or less with chlorinated compounds, which adhere with the utmost tenacity.

Several patents have also been claimed for the production of peroxide by dry oxidation, but all more or less yield an impure compound, or present difficulties in controlling the temperature. Taking into account the various difficulties thus set forth, the author, after a varied experience with the above product, recommends the following synthetical mode, which, besides being perfectly under control, possesses the advantage of offering a pure and theoretical yield, free from secondary products:—

In order to bring about the reaction, either litharge or sulphate of lead from vitriol tanks, &c., is introduced into canvas bags, through which is inserted a lead sheet. These bags are now immersed in dilute vitriol, and connected respectively to sheets of iron; the sulphate or other plumbic compound contained therein is thus speedily and completely reduced to the spongy metal, the bags being afterwards connected alternately by their lead plates and exposed to an electric current, the positives being thus completely converted into peroxide, whilst

the temporary accumulator thus produced is again emptied of its current into further quantities of spongy metal, thus manufacturing a further quantity of peroxide. The process thus set forth, when rightly conducted, yields an absolutely pure oxide, on a cheaper scale than those hitherto recommended.

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# SEPARATION OF MERCURY FROM ARSENIC, ANTIMONY, AND COPPER, BY IGNITION IN A CURRENT OF OXYGEN.

## By P. JANNASCH.

*A. Previous Precipitation by Sulphuretted Hydrogen, and Oxidation of the Filter with Fuming Nitric Acid in Tubulated Apparatus.*

### 1. Separation of Antimony and Mercury.

IN continuation of the separation of mercury and tin effected according to the above method (*Zeitsch. Anorg. Chem.*, xii., p. 132), I have, in concert with H. Heidenreich, succeeded in effecting the separation of mercury from arsenic, antimony, and copper.

The basis of the separation of mercury and antimony is a cautious combustion of the filter freed from the precipitate of sulphide by strong fuming nitric acid (1·4 to 1·5 sp. gr.), and also a complete conversion of antimony sulphide into antimonyl antimoniate. For this purpose the mixture of sulphide, previously collected and washed, is completely dried at 95°; the precipitate is next neatly dissolved away from the filter, which is then set aside in a flat-covered capsule of Meissen porcelain. The empty filter divided in slips is rolled up into rods, thrown into the apparatus, and fuming acid is then gradually added so as to fill about the fourth part of the main tube, and dissolved by agitation and holding the tube in hot water (in a deep capsule), whereon the evaporation of the excess of acid is effected in a current of dry air or carbonic acid over phosphoric acid, for this time only at 90° to 100°. The residue, which has generally a blackish colour, is repeatedly taken up in a similar quantity of nitric acid, and dried as above. After rinsing out the tube with water, the total precipitate, well comminuted with a platinum spatula, is introduced into the apparatus, diffused therein, and moistened with dilute nitric acid, which is simultaneously applied with a washing-bottle for rinsing away any particles which have mechanically adhered to the porcelain.

For the further oxidation of the mixture of sulphides the necessary quantity of ordinary strong nitric acid is dropped in at intervals, and it is again dried over phosphoric acid. The residue is finally further treated twice with the strongest fuming nitric acid in order to complete the oxidation, finally raising the heat each time to 150° to 180°, which especially promotes the completeness of the combustion.

Now follows the ignition in the current of oxygen. The receivers intended to take up the mercury are charged with dilute nitric acid. We ignite at first with a flame of only medium height, proceeding from the front backwards, and finally heating more strongly with the full flame, using at the same time a Bunsen burner to drive over the products of distillation. During such an oxidation of the precipitate not the slightest trace of antimony is sublimed. It is recommended to allow the ignited apparatus to cool very slowly, when the SbO₂ obtained is weighed at once.

In order to secure accurate results the following precautions must be especially observed :—Firstly, the current of oxygen must not be too lively at first, in order that minute particles of antimony binoxide may not be mechanically carried along. Further, we must ignite more strongly at the end, for the complete expulsion of the mercury. In the quantitative cleansing of the main receiver (spirting out the distillatory tube with hot dilute nitric acid, &c.) we must not overlook minimum particles of metallic mercury, which, on account of their great density, may easily be kept back, and we must pour afterwards into the evaporating capsule 10 to 15 c.c. of hydrogen peroxide. This latter substance exerts a remarkable influence on the solution of the metallic mercury, which at a certain degree of concentration proceeds quite rapidly and smoothly, which is otherwise effected at the end of the concentration only by the joint action of strong nitric and sulphuric acid. It may likewise happen that from the evaporated residue, on the addition of water, a basic salt is deposited, which can be completely re-dissolved only by prolonged heating with dilute hydrochloric acid. If particles of cork have to be filtered off, the washed filter should not be turned by sulphuretted hydrogen water.

The antimony dioxide, weighed direct in the apparatus and absolutely fixed on ignition, has a yellow colour when hot, and when cold white or greyish white. If we wish to withdraw it completely out of the tube, or weigh the antimony as $Sb_2S_3$, we fuse it with 8 to 10 parts of sulphur iodide (10 to 15 per cent of iodine) in a current of dry hydrogen sulphide, expel the excess of sulphur, and heat the residual antimony sulphide in a current of bromine.

### 2. Separation of Mercury from Copper.

About 0·5 grm. copper sulphate and 0·2 grm. mercuric chloride were dissolved in excess of hydrochloric acid diluted to 250 c.c. with warm water, with the addition of 5 c.c. concentrated sulphuric acid, precipitated whilst hot with hydrogen disulphide, filtered, washed, and dried at 95°. The precipitate is separated from the filter, and the latter is incinerated on a weighed tubulated apparatus with oxygen gas, the cuttings of the filter being carefully heated with the free flame.

After complete incineration the whole of the precipitate is added, and heated in a moderate current of oxygen, at first gently and finally strongly, until all the mercury has been driven over. The receivers are filled with dilute nitric acid to which bromine water had been added.

If the copper oxide is to be weighed in the tube, it must be ignited until the weight is constant, keeping in mind the experimental fact that the last traces of sulphuric acid are retained rather obstinately. Oxide of copper thus heated and dissolved in hydrochloric acid gives no reaction for sulphuric acid with a solution of barium chloride; but without igniting to a constant weight, the residual oxide, still occluding traces of sulphuric acid, may be dissolved in a little hot nitric or hydrochloric acid, and this liquid can be precipitated with soda in the known manner.

The liquids in the receivers are rinsed into a porcelain capsule and evaporated almost to dryness, then completely re-dissolved in hydrochloric acid and much water, filtered if needful, and precipitated with hydrogen sulphide whilst hot. The mercury sulphide is weighed upon a filter as usual. We have found it practicable to expel the carbon disulphide (after extraction of the sulphur mixed with precipitate) by means of ether.

*B. Ignition of the Mixture Evaporated to Dryness with Acetic Acid and Magnesia.*

### 3. Separation of Arsenic and Mercury in presence of an Excess of Magnesia.

0·3 grm. of mercuric oxide and 0·2 grm. arsenic teroxide (after extra solution of the arsenic in a few drops of soda-lye) are dissolved, at the temperature of the water-bath, by dilute nitric acid, and then dried over phosphoric acid at 120° in a current of air. This mixture is taken up with a few drops of water, 0·6 grm. of pure magnesia (free from chlorine) added, well mixed by shaking up, and again evaporated at the same temperature over phosphoric acid. Finally, it is again heated for about an

hour in a slow current of air to about 180° until all the moisture is expelled. The tube is then lifted out of the phosphoric acid bath, allowed to cool, the outside is cleansed with water, dried, and connected with the oxygen gas-holder and the drying apparatus. It is heated at first very gently with a small flame until the last trace of mercury is removed, afterwards more strongly, and at last with the full flame, in order to drive all the mercury into the receivers which contain dilute nitric acid and 15 c.c. of hydrogen peroxide. After the distillation is completed and the tube cooled, which must be done by gradually screwing down the flame, the fixed residue is dissolved in 5 c.c. concentrated hydrochloric acid, rinsed into a beaker, 3 grms. citric acid added, and finally supersaturated with an excess or strong ammonia. The precipitate of ammonium magnesium arseniate is treated in the known manner, as is also the liquid from the receivers containing all the mercury.—*Zeit. Anorgan. Chem.*, xii., 359.

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## A NEW METHOD FOR THE ESTIMATION OF IRON OXIDE AND ALUMINA IN PHOSPHATE ROCK.

### By THOMAS S. GLADDING.

THE method for the separation of alumina from phosphate of lime by three successive precipitations with ammonium acetate is tedious, though accurate if proper precautions be taken, as shown in a former paper on this subject (*Journ. Am. Chem. Soc.*, xviii., 717; CHEM. NEWS, lxxiv., 112).

The following modification suggested itself as saving both time and labour. This modification consists of the separation of alumina from calcium phosphate and iron by means of its solubility in an excess of caustic potash. To demonstrate the accuracy of this method, a solution of ammonia-alum, 20 grms. in a litre, was used as in the previous experiments, 10 c.c. containing 0·0225 grm. $Al_2O_3$. The caustic potash solution was made by dissolving 500 grms. of caustic potash in distilled water and diluting to one litre. Chemically pure caustic potash, purified by barium, was used, and was carefully tested for alumina, as much so-called chemically pure potash contains an appreciable amount of alumina.

To a solution of mixed phosphates of alumina, iron, and lime were added 15 c.c. of the C.P. potash solution. The mixture was digested for an hour at a temperature of 70° C., with occasional stirring. It was then filtered, the filtrate neutralised with hydrochloric acid, and the alumina was precipitated as a phosphate with ammonium acetate, as described in my ammonium acetate method.

Ten c.c. of standard alumina solution + 0·030 grm. iron oxide + 0·500 grm. calcium phosphate gave—

|   | $Al_2O_3.P_2O_5$ found.<br>Grm. | $Al_2O_3$.<br>Grm. |
|---|---|---|
| 1 | 0·0538 | 0·0225 |
| 2 | 0·0542 | 0·0227 |
| 3 | 0·0543 | 0·0227 |
| 4 | 0·0543 | 0·0227 |

Comparative tests were made on phosphate rocks between this method by solution in C.P. potash and by three successive precipitations with ammonium acetate.

|   | By new potash method.<br>$Al_2O_3$ found.<br>Per cent. | By acetate method.<br>$Al_2O_3$ found.<br>Per cent. |
|---|---|---|
| 1 | 1·05 | 1·03 |
| 2 | 1·19 | 1·16 |
| 3 | 1·86 | 1·61 |
| 4 | 1·07 | 0·99 |
| 5 | 1·88 | 1·98 |

These results show the accuracy of this method, both in obtaining a known amount of alumina and in showing close agreement with results by the acetate method.

This method has been in use in our laboratory for over a year. A reprint of an article by M. Henri Lasne (*Bull. de la Soc. Chim, de Paris*, [3], xv., 118, 1896) has just been received, giving a method for the separation of alumina from phosphates of iron and lime very similar to this. M. Lasne uses caustic soda instead of potash, and precipitates his aluminum phosphate with ammonium hyposulphite instead of ammonium acetate. I have made a few comparative tests by my method and that of M. Lasne, and find closely-agreeing results.

Using 10 c.c. standard alumina solution + 0·500 grm. calcium phosphate I found—

|   | By my method. | | By Lasne's method. | |
|---|---|---|---|---|
|   | $Al_2O_3.P_2O_5$.<br>Grm. | $Al_2O_3$.<br>Grm. | $Al_2O_3.P_2O_5$.<br>Grm. | $Al_2O_3$.<br>Grm. |
| 1 | 0·0542 | 0·0220 | 0·0540 | 0·0226 |
| 2 | 0·0538 | 0·0225 | 0·0533 | 0·0223 |

In the analysis of a phosphate rock I found—

| By my method.<br>$Al_2O_3$ found. Per cent. | By Lasne's method.<br>$Al_2O_3$ found. Per cent. |
|---|---|
| 1·75 | 1·73 |
| 1·80 | — |

The detailed method used in my work is as follows :— Treat the finely-ground rock phosphate with a magnet to remove any metallic iron derived from the iron mortar used in the preparation of the sample. Dissolve 4 grms. of the rock in 30 c.c. dilute hydrochloric acid (1—1), heating just below the boiling-point for half an hour. This prevents the solution of pyrites. Filter into a 200 c.c. flask, add a few drops of nitric acid, and boil to oxidise the iron, cool, and dilute to mark. Take 50 c.c. containing 1 grm. of rock and run into 20 c.c. of the solution of C.P. caustic potash. Digest for an hour at 70° C., stirring occasionally. Let the precipitate settle, and filter on a large paper, first decanting the supernatant liquid on the paper and finally washing on the precipitate. Wash two or three times with hot water.

To the filtrate add one grm. of ammonium phosphate, acidify with hydrochloric acid, add ammonia until a permanent precipitate is formed and dilute hydrochloric acid, drop by drop, until it is just dissolved. Add a mixture of 15 c.c. neutral ammonium acetate solution and 5 c.c. acetic acid (30 per cent) and digest for half an hour at 70° C., by which time the precipitation is complete.

Filter, washing five or six times with hot ammonium acetate solution (10 per cent), stirring up the precipitate with the jet each time. Ignite with a low flame until the paper is charred, increase the heat, and, when the paper is completely consumed, blast for a minute. The precipitate is the normal aluminum phosphate, and its weight multiplied by the factor 0·418 gives the $Al_2O_3$.

The iron oxide is determined volumetrically, preferably by the bichromate method, in a solution of the precipitate of iron oxide and calcium phosphate thrown down by the caustic potash. It is also determined separately, by the same method, in a solution of 5 grms. of the rock in dilute hydrochloric acid (1—1).

My thanks are due to Mr. H. E. Cutts, A.M., for valuable assistance in the above investigation.—*Journal of the American Chemical Society*, xviii., No. 8.

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ON THE

## AMOUNT OF GOLD AND SILVER IN SEA-WATER.*

By A. LIVERSIDGE, M.A., F.R.S.,<br>Professor of Chemistry in the University of Sydney.

IN the following paper are given the results of some experiments made with the object of determining the amount of gold in the sea-water off the coast of New South Wales.

* Read before the Royal Society of N. S. Wales.

The only reference that I can find in Sydney libraries relating to the presence of gold in sea-water are those of Sonstadt (CHEMICAL NEWS, xxvi., pp. 159, 160), which will be made use of later on in this paper, and a reference by Dr. T. Sterry Hunt ("Chemical and Geological Essays," London, 1879) to a Paper read before the American Association for the Advancement of Science, in 1866, by Professor Wurtz, in which he expressed an opinion that gold would be found in sea-water; but I cannot trace Prof. Wurtz's paper.

Then in 1894, Mr. E. C. C. Stanford, President of the Society of Chemical Industry, in his Address to the Members (*Journ. Soc. Chem. Ind.*, xiii., July 31, 1894, p. 697), stated:—"The presence of gold has not been satisfactorily proved; it was expected it might accumulate in the copper sheathing of ships, and Messrs. Muntz obliged me with specimens of old sheathing, both copper and Muntz metal. Mr. Inglis, who kindly examined these for me, found both gold and silver, but not in larger proportion than usual."

The results were, per ton:—

| | Copper Sheathing. | | | Muntz Metal. | | |
|---|---|---|---|---|---|---|
| | Ozs. | dwts. | grs. | Ozs. | dwts. | grs. |
| Gold | 0 | 2 | 21 | 0 | 1 | 15 |
| Silver | 4 | 12 | 9 | 5 | 3 | 12 |

Professor Judd, F.R.S., informed me that a Paper upon this subject was published in a Norwegian journal by Münster, about 1891, but I can find no reference to it in our Sydney libraries.

Sonstadt, in his Paper on the " Presence of Gold in Sea-water," gives various methods for the detection of the gold, and in a later letter to the CHEMICAL NEWS (vol. lxv., p. 131) refers to his previous communication of 1872, and states that the amount of gold is " far less than 1 grain per ton."

His first process is as follows :—Two or three decigrms. of pure ferrous sulphate are dissolved in the water, which is acidulated by 2 or 3 drops of hydrochloric acid. The solution is heated in a *chemically clean* well-glazed porcelain dish, over a small flame, so managed that the flame may touch the under part of the dish without causing ebullition. Under these circumstances a lustrous film of iron oxide forms in the dish, commencing from the portion directly heated by the flame. The heat is continued, without boiling, until the sea-water is evaporated to about half, or so long as the film increases in extent and in lustre. The liquid is then poured off, the strongly adherent film is rinsed with a little water; and then about 50 c.c. of strong chlorine water is allowed to stand in the dish for an hour or two, after which it is slowly evaporated down (over the film) to a few drops, a drop of dilute hydrochloric acid being added towards the end of the evaporation. The liquid, which should be nearly colourless, is then poured into a test-glass containing a few drops of solution of stannous chloride, when, after a few minutes, the liquid takes a bluish or purplish tint, which may be exactly matched by a drop or two of a suitably diluted solution of gold added to a corresponding portion of tin-salt in another glass."

The sea-water first examined was collected from the coast at Coogee, away from any fresh water or other drainage. Eleven trials of this water were made with 200 c.c., as recommended by Sonstadt, but no trace of a purple or even pink tint was obtained, but with 600 c.c. a faint amethyst tint was obtained after standing some time. As a rule, after adding the stannous chloride, a white or grey precipitate came down in the course of a few days, and this precipitate in many cases became pink, purple, or slate-coloured.

To check Sonstadt's method various experiments were carried out. Gold chloride (from pure metal dissolved in chlorine water) was added to Coogee sea-water in the proportion of 1 grain of gold to the ton, and 200 c.c. of this was treated by Sonstadt's process on March 19th,

1895, when a light brown precipitate was thrown down by the stannous chloride; on the 27th the precipitate was of a red colour below with a pale pink layer above; on the 3rd of April the pink tint was more decided. Hence, if allowed to stand for a few days, the test will detect in 200 c.c. the presence of added gold in the proportion of 1 grain to the ton of sea-water, the gold originally present only being recognisable in 600 c.c.

On December 11th, 1894, a litre of the Coogee sea-water was concentrated and the test applied; no trace of pink or purple appeared, but on February 8th, 1895, a slight brown sediment had formed, which may have been due to gold.

Next, 2 litres were treated on December 28th, 1894, and allowed to stand until February 8th, 1895, when a faint pink tint was observable on the surface of the white precipitate. The second chlorine water extract of the film yielded a white precipitate which also had acquired a pink tint on February 8th.

On August 14th, 1895, two more samples, each of 2 litres of Coogee water, were tested. On the 15th the precipitates were brownish; the brownish tint seems to be due to the presence of gold. The contents of the two test-tubes were mixed together, dried, and scorified with 250 grains of assay lead free from gold, when a small bead of gold was obtained.

Sonstadt's second method was also tried, *i. e.*, with barium chloride, as follows :—" From half a litre to a litre of sea-water should be taken for the experiment. As much solution of pure chloride of barium is added to the water as will give a grain of precipitate. A day or two should be allowed for the precipitate to settle. The precipitate is collected, dried, mixed with borax and lead, and the button of lead obtained before the blowpipe on charcoal is cupelled. The bead obtained is yellowish white, of the same colour as an alloy of sixty parts of gold to forty parts of silver, or thereabout. For confirmation of the presence of gold the bead may be dissolved in a very small test-tube, in a few drops of aqua regia, which is then evaporated, at a gentle heat, nearly to dryness. A few drops of pure hydrochloric acid are added, and the solution again evaporated, to destroy the excess of nitric acid. The solution is evaporated very nearly, but not quite, to dryness, a few drops of water are added, and the mixture warmed, and, when the chloride of silver is settled, a drop of solution of stannous chloride is allowed to fall down the side of the tube into the liquid, when the characteristic gold reaction is obtained."

Sonstadt's barium chloride method was tried on sea-water from off Jervis Bay as well as from the coast of Coogee, but the yield of gold was either much less than by the ferrous sulphate method (see further on) or no gold at all was obtained, even when two or more litres were used. Similar results were obtained from the use of stannous chloride and mercuric chloride together. Mercuric chloride alone and afterwards precipitated by hydrogen sulphide gave fairly good results. It was thought that the previous addition of sulphurous acid, oxalic acid, and other reducing substances, might increase the amount of gold obtained, but this was not found to be the case,—on the contrary, the yield was reduced.

As the result of a very large number of experiments with the film test upon gold chloride in distilled water and in sea-water, it was found that—

1. All the gold is not carried down by the film—not even by repeating the process and obtaining a second film; a little gold still being obtainable by a third film.

2. Neither is all the gold extracted by one treatment of the film with chlorine water.

3. Some of the gold is left on the dish in evaporating the chlorine water solution.

4. Several days and even weeks were required, in many cases, for the colour reaction to appear.

*Gold in Sea-water along the Coast of New South Wales.*

Next, a set of experiments was made upon water collected out at sea: twelve samples, two Winchester quarts of each, were kindly collected for me by Captain Hutton, of the N. S. Wales Government steamer *Thetis*, by direction of Mr. C. W. Darley, then Engineer-in-Chief for Harbours and Rivers, to whom my thanks are due for the ready assistance he has given me in this and other similar matters. Prior to being sent out the bottles were carefully cleaned, numbered, and packed in cases (each holding two bottles) so as to ensure purity and prevent error, and each bottle was rinsed with sea-water when about to be filled.

(To be continued).

# NOTICES OF BOOKS.

"*Made in Germany.*" By ERNEST EDWIN WILLIAMS. London: William Heinemann.

THE most appropriate motto for this work would be—

    "'T is true, and pity 't is 't is true."

Mr. Williams enters upon his needful but thankless task with a survey of the "Departing Glory." What is the "glory" which is departing, and whose it was, needs little demonstration, and can scarcely be refuted by calling the author a Cassandra, whose prophecies of evil turned out to be true in the end.

The decline of our national industries is next discussed, under the heads of "Iron and Steel," "Ships, Hardware, and Machines," "Textiles," "Chemicals," and the "Lesser Trades." Then come the decisive questions, why Germany beats us? what must we do to be saved? The answers to these questions are manifold: lower wages and longer hours of labour are considered first, and are admitted to be causes, though not the one and greatest cause, of British decline and of alien success. The author contends that "the shortening of the hours of labour not unfrequently results in increased productivity." This is quite true up to a certain limit. A man may do more work in ten than in twelve hours, but can he do more in eight than in ten hours?

Strikes he recognises as one of the causes of our insuccess; but he fails to discriminate between the classes of strikes. If by their means the supply of some indispensable article is suspended,—*e. g.*, the output of coal, —the mischief is incalculable, and falls upon a variety of arts.

The denunciation of German goods as "billig und schlecht"— or as it here misprinted "blessig und schnell"—is fast losing its truthfulness.

The "Merchandise Marks Act" of 1897 is quoted as one of the causes of successful German competition. The author thinks rightly, that either "the Act is not wanted at all, or it does not go far enough," but he notices that "anyhow it makes for honesty." And in the alien success which he deplores honesty is greatly lacking. We know that a middleman, a traveller, calling upon a consumer in another foreign country, has been known to offer as British goods not manufactured in Britain at all, and of a decidedly inferior quality. When these are complained of, the vendor, with seeming candour, admits that British products have of late fallen off in quality, and suggests that German products will give more satisfaction. If an order is obtained, a list of German goods is sent in purposely of a better quality than those ordinarily "made in Germany," and so the thin end of the wedge is inserted.

Another stratagem is often tried where a British firm is induced, by boasted "intellectual interest," to employ alien clerks and book-keepers. Passing a ploughed field in the West Riding, our eyes fell upon a sheet of MS. It contained a list of the names and addresses of important firms in South America, annotated with the peculiar predilections of each, in the style of packing up goods. The language and the characters were German, and the document was obviously intended to have been sent to some German agent or middleman.

Conveyance of goods is one of the factors in undermining the British manufacturer. For a ton of the same class of goods he has often to pay more per mile on an English railway than do alien goods of the same kind, for the same distance, on the same line. Thus a bounty is given to the enemy! Even some of our own colonies grant differential rates in favour of the alien.

Education is a remaining factor. We professed, some score of years ago, to be struck with the ignorance of our own people, and, at the cost of millions untold, we have been striving to force elementary literary education upon that part of our population which least needs it. Our manufacturers, our managers, overlookers, and the like, are the class who most need a higher training. The rank and file of the industrial army with us are quite as well educated as their continental opponents. What we want cannot be obtained from Board Schools.

We most strongly advise all intelligent and patriotic Englishmen to study this book carefully, and lay its lessons to heart.

*Catalogue of Chemical Apparatus, &c., and Chemicals* Manufactured and Sold by PHILIP HARRIS and Co., Ltd., Edmund St., Birmingham.

IF we may judge from the number of firms who issue price lists of apparatus and chemicals, we must be moving in the right direction as far as chemical research and chemical industry are concerned. We fear, however, that on too many of the articles would appear the mark "made in Germany."

The Catalogue is rich in balances. In addition to the well-known instruments of Oertling we find, figured and described, those of Bunge, Becker, Kuhlmann, and Sartorius.

No sets of decimal weights seem to be procurable in which the subdivisions of the gramme are made of bent wires, and in sets of 6, 3, 2, and 1, which is much more convenient than 5, 5, 2, 2, 1, as it involves the handling of fewer pieces.

Among burettes the instrument of Binks still maintains a place.

Gas analysis is evidently becoming more appreciated, and hence there is a growing variety of apparatus for its performance, such as Bunte's, Hempel's, Elliott's, the Orsat-Lunge, Orsat-Pryce, and Orsat-Müncke, which last is apparently made only by Philip Harris and Co.

Several forms of microscopes are here mentioned, and, what is a novel and very satisfactory feature, spectroscopes also are not ignored, as we too often see.

Lovibond's tintometer is very fully described, but singularly not under the head of colorimeters.

Jena glass figures prominently, and seems now under most circumstances superior to the time-honoured product of Bohemia.

The selection of reagents and other chemicals is very full, and will be found very useful to persons engaged in research. A few points, however, are rather perplexing. Thus we find among the aniline colours "fuschine" priced per ounce 2s., as against "magenta" (best) 10d., and rosaniline acetate 1s. 6d. These substances, as the names are commonly applied, ought to be identical. Whence, then, the difference in price? Eosine among the aniline colours is marked 1s. 2d. per ounce, and in another part of the Catalogue 1s. 6d.

Among rarities we note tellurium 28s. per grain, rubidium (metallic) 4s. 6d. per grain, cerium 1s. 6d. per grain.

There is a very full supplemental list of the gas devices of Fletcher (now Fletcher, Russell, and Co., Ltd.). Such

of these appliances as we have had occasion to use have proved very satisfactory.

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*The Speed of Propagation of the Rays of Gravitation, and the Laws of their Action.* (" Die Fortpflanzungs, Geschwindigkeit der Schwerkraftstrahlen und deren Wirkungsgesetze "). By RUDOLF MEWES, Engineer and Physicist. Berlin: M. Kroyn, (Fischer's " Technologischer Verlag "). 1896. Pp. 96.

THE author is to a certain extent developing the ideas laid down by Christian Huyghens. From considerations which the mathematician alone can duly appreciate, he comes to the conclusion that the molar attraction is merely an especial form of the ethereal oscillations of heat, and that this physical force is the prime cause of all other forms of energy, the latter, according to the nature of the existing medium, appearing to us as light, electricity, and in general molecular attraction and general attraction of masses.

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*Hongkong. Report of the Government Analyst.* June 20, 1896.

THE Government Analyst, W. E. Crow, states that 245 articles have been examined in the Government Laboratory. These included 11 toxicological cases, 53 potable waters, 168 petroleum, 4 milk, 23 cases under the morphine ordinance, 17 alcoholic liquors, and 29 miscellaneous articles. The toxicological cases included three attempts of human poisoning, one of which proved fatal. The drug used was the root of Tün Cheang ts' ó (*Gelsemium elegans*).

Orpiment (arsenic tersulphide) was used in an attempt to poison six men of No. 3 Section, A Company, Hongkong Regiment. The specimen examined contained 33·74 grains of arsenic tersulphide, a substance easily procurable in the Far East. All the patients recovered. In the remaining case—apparently not fatal—the drug used was probably the active principle of *Datura alba* (Nau yung, &c.). The offender was convicted.

The samples of water from the Frokfollom, Tailum, and Kowloom supplies were all found excellent, but many of the town wells were highly polluted. The wells are, in many cases, merely holes in the ground, a few feet deep, lined with loose granite block.

The samples of milk are pronounced excellent, " even as compared with the best dairy samples obtained in Britain."

Of the alcoholic liquors, one is " said to have been prepared from the penes of three animals and hartshorn " ( ! ).

The laboratory has been refitted, and is supplied with two balances by Becker and one of the Robeval type.

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*General Scientific Congress of Chile of* 1894. (" Congreso Cientifico General Chileno "). Santiago de Chile : Cervantes. 1895.

THIS publication gives an account of a late meeting of a body which has a strong resemblance to the British Association. Its sections number nine, to wit :—1. Mathematics, Pure and Applied. 2. Physical and Chemical Sciences. 3. Medicine and Pharmacy. 4. Biology. 5. Geology and Mineralogy. 6. Geography, Physical and Astronomical. 7. History, Philology, and Ethnology. 8. Psychology and Pedagogics. And lastly, 9, Sociology, Law, and Political Economy.

To us the last three sections seem very much out of place, though on this subject we must speak mildly so long as our British Association retains its deplorable section for Statistics and Economy. We must note that the Chilian Association, in its 8th rule, stipulates that political or religious questions " may not be discussed in any section." To obey this rule we suggest that Sect. 9 should be eliminated.

The sections are classified under three groups. In the first of these figure, along with mathematics, physics, chemistry, geology and mineralogy, physical geography and astronomy. In the second, biology is worked along with pharmacy and medicine.

Among the principal papers read are " Chemical Investigations on *Margarodes vitium*," by Dr. Narciso Briones; " Influence of Chlorine on Ores of Gold and Silver," by Fernando Gautin ; " Observations on the Normal Composition of the Well-waters of Santiago," by Pablo Letemeyer ; and " Accidents caused by Venomous Insects in Chile," by Dr. Francisco C. Guzman.

" Spelling reform " seems to be attacking the Chilians in an aggravated form.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 8, August 24, 1896.

**Electric Convection following the Lines of Force produced by Röntgen's Rays.**—Auguste Righi.—In my various publications on the electric phenomena produced by the X rays I have always interpreted the facts observed as if it was demonstrated that the mechanism of the propagation of electricity is the same as on the dispersion by sharp points, or the dispersion on the surface of conductors heated to redness, or the dispersion produced by the ultra-violet rays. I reserve it to myself to show, in a memoir comprising the whole of my researches on these phenomena, in whatever manner the electricity is propagated in gases traversed by these rays. I think it well to make known at present some experiments which appear to me conclusive. It seems to me that the experiments clearly show the existence of a connection following the lines of force, and thus confirm my old views on the mechanism of the propagation of electricity in gases. I am happy to notice the agreement between my view and that which has been recently formulated by M. Villari. This physicist infers from his ingenious experiments that the dispersion produced by the X rays is a convection.

**Utility in Radiography of Screens of Phosphorescent Zinc Sulphide ; the Emission by Glowworms of Rays Traversing the Needle Paper.**—Charles Henry. —I substitute for the simple fluorescent screens of barium platinocyanide, calcium tungstate, &c., a screen of my phosphorescent zinc sulphide, covered with a leaf of " needle paper," and I lay on the paper the object to be radiographed. After some minutes' exposure to the radiation of the Crookes tube I remove the screen into the dark chamber ; the depressions of the objects, opaque to the X rays, appear black and the transparent parts appear light. I can study the minutest details of the image for a quarter of an hour at least. On gently heating the screen with a source of dark heat I can continue this examination longer. This method, which allows of a great economy of electric energy and of tubes may be recommended for exhibitions, lectures, and all cases where it is not required to preserve the radiographic specimen. Phosphorescent zinc sulphide is incomparably more sensitive to the X rays than is calcium sulphide. If we expose for five minutes to one and the same radiation from the tube a plate enamelled with calcium sulphide and a screen of zinc sulphide, the former scarcely shines, whilst the latter is near its luminous saturation. During the last evenings I have had occasion to place during times varying from half an hour to several hours, some glowworms upon photographic plates wrapped up in needle-paper : on developing we could distinguish on the plate black and

white tracks which reproduced exactly the course pursued by the subventral lanterns of these capricious animals.

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*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 5, Vol. i., No. 7.

**Review of a Treatise by L. Holborn and Willy Wien on the Determination of High Temperatures.—** R. Maesse.—This treatise cannot be reproduced without the eleven accompanying figures. The author's conclusions are as follows:—1. The measures of temperatures by means of observations of resistances are less exact than those effected with the thermo-electric couple, platinum-rhodium-platinum. If we check the resistance in the cold after each measurement, we often observe important variations. As the coefficient of temperature also varies this reaction can offer little guarantee. 2. Callendar's formula does not explain the facts with such accuracy that we could found upon it extended extrapolations. 3. The thermo-electric couple may be easily compared with the air thermometer, since it may be without difficulty introduced into the recipient of the latter. Even if the temperature is not very uniformly distributed in the furnace, the couple takes exactly the temperature of the mass of air of the thermometer.

## MISCELLANEOUS.

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**The South-West London Polytechnic Institute, Chelsea.**—This institute was only opened last October, and already some 1400 students have availed themselves of its educational advantages. The work hitherto has been mainly in the evening, but on September 29th the Institute will be opened to Day Students in Mathematics, Mechanics, Mechanism, Architecture, and Building Construction, Drawing Office Work, Workshops, Electrical Technology, Physics, Physical and Electrical Laboratories, Chemistry, Chemical Laboratory, and Applied Art. The hours will be from 10 a.m. to 1 p.m., and from 2 to 5 p.m. on each working day, except Saturday, when the hours will be from 10 a.m. to 1 p.m. The student may, for a very moderate fee, go through a complete course of Electrical Engineering, Mechanical Engineering, Architecture, Technical Chemistry, Applied Art, and Colonial Training, in two years, provided he can devote his whole daytime to the work. If he cannot devote his whole time in the day to the work, the classes are so arranged that he may, nevertheless, go through a precisely similar course in three, four, or more years; and as similar courses are provided in the evening, the opportunity is afforded him of shortening the period by attending evening as well as day classes. The education will be given partly by lectures and exercise classes, but mainly through the laboratory and workshop practice of the students themselves.

**Programme of the Royal Technical High School at Aachen.**—For the year 1896-97, October 1st to July 31st.— The curricula in this institution are not merely exceedingly complete, but are capable of being modified according to the destination of each student. There are courses for Architects, Constructive Engineers, Surveyors, Mechanical Engineers (with a view to Electro-technics), Mining Engineers (for the service of the State and for private undertakings), Metallurgists, Chemists, and Electrochemists. Each course is arranged for four years. The curriculum for Chemists includes:—Construction of buildings, technology, organic experimental chemistry, inorganic experimental chemistry, chemistry of metals, national economy, higher mathematics, mechanics, and experimental physics. In the second year follow:— Technology, encyclopædic doctrine of machines, building machines, crystallography and mineralogy, exercises in determining minerals, chemistry of benzene and pyridine, volumetric analysis, study of salt springs, technical chemistry, and for food chemists, botany (general, special, and microscopic). In the third year follow:—Introduction into the metallurgy of iron and of other metals, general geology, doctrine of strata, installation of chemical works, practice in microscopic botany (for food chemists), practical telegraphy and telephony. In the fourth year follows the theory of electro-chemistry. In a parallel column is mentioned industrial hygiene and a number of subjects which appear to us simply a waste of time and of brain-power, *e.g.*, history of national economy, select chapters on statistics, the German law on bills of exchange, German insurance of workmen, doctrine of finance, and encyclopædia of law. Under the conditions which prevail in Britain, we should pronounce the study of finance, statistics, the law of bills of exchange, and financial doctrines, an utter waste of time for the chemist. The only legal matters with which he may advantageously concern himself are patent law and perhaps toxicology. We think that the questions of the water supply of towns and the treatment of waste waters, domestic and industrial, belong to the chemist, and not to the engineer. We do not see that in the studies required for the chemist sufficient weight is laid on the use of the microscope and the spectroscope.

**Questionable Application of Science.**—In a technical contemporary we find the following passage, which, whether its assertions are true or false, claims the attention of analysts:—"Scientific training seems very often to be diverted into curious channels. A large calico-printer recently informed us that the chemical knowledge of the German drug and dyestuff manufacturers seemed to be devoted entirely to the art of defeating tests rather than to the manufacture of drugs to pass genuine muster. It was the Germans who introduced that dangerous adulterant in Portland cement—gypsum, to wit,—entirely with a view to circumventing the American tests for cement. It matters not to the Germans that their cement is rendered dangerous, and that better results can be attained by safe means at very trifling cost. They have found an adulterant to serve a merely temporary purpose, and that is all they care to do. The Japanese seem to be following on similar lines. It would be amusing were it not so pitiable."

# THE CHEMICAL NEWS.

VOL. LXXIV., No. 1922.

## BRITISH ASSOCIATION
### FOR THE
## ADVANCEMENT OF SCIENCE.

LIVERPOOL, 1896,

### INAUGURAL ADDRESS OF THE PRESIDENT,
SIR JOSEPH LISTER, BART., D.C.L., LL.D., F.R.S.

(Concluded from p. 143).

I ASK your indulgence if I have seemed to dwell too long upon matters in which I have been personally concerned. I now gladly return to the labours of others.

The striking results of the application of the germ theory to Surgery acted as a powerful stimulus to the investigation of the nature of the micro-organisms concerned; and it soon appeared that putrefaction was by no means the only evil of microbic origin to which wounds were liable. I had myself very early noticed that hospital gangrene was not necessarily attended by any unpleasant odour; and I afterwards made a similar observation regarding the matter formed in a remarkable epidemic of erysipelas in Edinburgh obviously of infective character. I had also seen a careless dressing followed by the occurrence of suppuration without putrefaction. And as these non-putrefactive disorders had the same self-propagating property as ferments, and were suppressed by the same antiseptic agencies which were used for combating the putrefactive microbes, I did not doubt that they were of an analogous origin; and I ventured to express the view that, just as the various fermentations had each its special microbe, so it might be with the various complications of wounds. This surmise was afterwards amply verified. Professor Ogston, of Aberdeen, was an early worker in this field, and showed that in acute abscesses, that is to say those which run a rapid course, the matter, although often quite free from unpleasant odour, invariably contains micro-organisms belonging to the group which, from the spherical form of their elements, are termed micrococci; and these he classed as streptococci or staphylococci, according as they were arranged in chains or disposed in irregular clusters like bunches of grapes. The German pathologist, Fehleisen, followed with a beautiful research, by which he clearly proved that erysipelas is caused by a streptococcus. A host of earnest workers in different countries have cultivated the new science of Bacteriology, and, while opening up a wide fresh domain of Biology, have demonstrated in so many cases the casual relation between special micro-organisms and special diseases, not only in wounds but in the system generally, as to afford ample confirmation of the induction which had been made by Pasteur that all infective disorders are of microbic origin.

Not that we can look forward with anything like confidence to being able ever to see the *materies morbi* of every disease of this nature. One of the latest of such discoveries has been that by Pfeiffer, of Berlin, of the bacillus of influenza, perhaps the most minute of all micro-organisms ever yet detected. The bacillus of anthrax, the cause of a plague common among cattle in some parts of Europe, and often communicated to sorters of foreign wool in this country, is a giant as compared with this tiny being; and supposing the microbe of any infectious fever to be as much smaller than the influenza bacillus as this is less than that of anthrax, a by no means unlikely hypothesis, it is probable that it would never be visible to man. The improvements of the microscope, based on the principle established by my father in the earlier part of the century, have apparently nearly reached the limits of what is possible. But that such parasites are really the causes of all this great class of diseases can no longer be doubted.

The first rational step towards the prevention or cure of disease is to know its cause; and it is impossible to over-estimate the practical value of researches such as those to which I am now referring. Among their many achievements is what may be fairly regarded as the most important discovery ever made in pathology, because it revealed the true nature of the disease which causes more sickness and death in the human race than any other. It was made by Robert Koch, who greatly distinguished himself, when a practitioner in an obscure town in Germany, by the remarkable combination of experimental acuteness and skill, chemical and optical knowledge, and successful micro-photography, which he brought to bear upon the illustration of infective diseases of wounds in the lower animals, in recognition of which service the enlightened Prussian Government at once appointed him to an official position of great importance in Berlin. There he conducted various important researches; and at the London Congress in 1881 he showed to us for the first time the bacillus of tubercle. Wonderful light was thrown by this discovery upon a great group of diseases which had before been rather guessed than known to be of an allied nature; a precision and efficacy never before possible was introduced into their surgical treatment, while the physician became guided by new and sure light as regards their diagnosis and prevention.

At that same London Congress Koch demonstrated to us his "plate culture" of bacteria, which was so important that I must devote a few words to its description. With a view to the successful study of the habits and effects of any particular microbe outside the living body, it is essential that it should be present unmixed in the medium in which it is cultivated. It can be readily understood how difficult it must have been to isolate any particular micro-organism when it existed mixed, as was often the case, with a multitude of other forms. In fact, the various ingenious attempts made to effect this object had often proved entire failures. Koch, however, by an ingenious procedure converted what had been before impossible into a matter of the utmost facility. In the broth or other nutrient liquid which was to serve as food for the growing microbe, he dissolved, by aid of heat, just enough gelatin to ensure that, while it should become a solid mass when cold, it should remain fluid though reduced in temperature so much as to be incapable of killing living germs. To the medium thus partially cooled was added some liquid containing, among others, the microbe to be investigated; and the mixture was thoroughly shaken so as to diffuse the bacteria and separate them from each other. Some of the liquid was then poured out in a thin layer upon a glass plate and allowed to cool so as to assume the solid form. The various microbes, fixed in the gelatin and so prevented from intermingling, proceeded to develop each its special progeny, which in course of time showed itself as an opaque speck in the transparent film. Any one of such specks could now be removed and transferred to another vessel in which the microbe composing it grew in perfect isolation.

Pasteur was present at this demonstration, and expressed his sense of the great progress effected by the new method. It was soon introduced into his own Institute and other laboratories throughout the world, and it has immensely facilitated bacteriological study.

One fruit of it in Koch's own hands was the discovery of the microbe of cholera in India, whither he went to study the disease. This organism was termed by Koch, from its curved form, the "comma bacillus," and by the French the cholera vibrio. Great doubts were for a long time felt regarding this discovery. Several other kinds of bacteria were found of the same shape, some of them producing very similar appearances in culture media,

But bacteriologists are now universally agreed that, although various other conditions are necessary to the production of an attack of cholera besides the mere presence of the vibrio, yet it is the essential *materies morbi ;* and it is by the aid of the diagnosis which its presence in any case of true cholera enables the bacteriologist to make, that threatened invasions of this awful disease have of late years been so successfully repelled from our shores. If bacteriology had done nothing more for us than this, it might well have earned our gratitude.

I have next to invite your attention to some earlier work of Pasteur. There is a disease known in France under the name of *choléra des poules*, which often produced great havoc among the poultry yards of Paris. It had been observed that the blood of birds that had died of this disease was peopled by a multitude of minute bacteria, not very dissimilar in form and size to the microbe of the lactic ferment to which I have before referred. And Pasteur found that, if this bacterium was cultivated outside the body for a protracted period under certain conditions, it underwent a remarkable diminution of its virulence; so that, if inoculated into a healthy fowl, it no longer caused the death of the bird, as it would have done in its original condition, but produced a milder form of the disease which was not fatal. And this altered character of the microbe, caused by certain conditions, was found to persist in successive generations cultivated in the ordinary way. Thus was discovered the great fact of what Pasteur termed the *atténuation des virus*, which at once gave the clue to understanding what had before been quite mysterious, the difference in virulence of the same disease in different epidemics.

But he made the further very important observation that a bird which had gone through the mild form of the complaint had acquired immunity against it in its most virulent condition. Pasteur afterwards succeeded in obtaining mitigated varieties of microbes for some other diseases, and he applied with great success the principle which he had discovered in fowl-cholera for protecting the larger domestic animals against the plague of anthrax. The preparations used for such preventive inoculations he termed "vaccins," in honour of our great countryman Edward Jenner. For Pasteur at once saw the analogy between the immunity to fowl-cholera produced by its attenuated virus and the protection afforded against smallpox by vaccination. And while pathologists still hesitated, he had no doubt of the correctness of Jenner's expression, *variolæ vaccinæ*, or smallpox in the cow.

It is just a hundred years since Jenner made the crucial experiment of inoculating with smallpox a boy whom he had previously vaccinated, the result being, as he anticipated, that the boy was quite unaffected. It may be remarked that this was a perfectly legitimate experiment, involving no danger to the subject of it. Inoculation was at that time the established practice; and if vaccination should prove nugatory, the inoculation would be only what would have been otherwise called for, while it would be perfectly harmless if the hoped-for effect of vaccination had been produced.

We are a practical people, not much addicted to personal commemorations; although our nation did indeed celebrate with fitting splendour the jubilee of the reign of our beloved Queen, and at the invitation of Glasgow the scientific world has lately marked in a manner, though different, as imposing, the jubilee of the life-work of a sovereign in science (Lord Kelvin). But while we cannot be astonished that the centenary of Jenner's immortal discovery should have failed to receive general recognition in this country, it is melancholy to think that this year should, in his native county, have been distinguished by a terrible illustration of the results which would sooner or later inevitably follow the general neglect of his prescriptions.

I have no desire to speak severely of the Gloucester Guardians. They are not sanitary authorities, and had not the technical knowledge necessary to enable them to judge between the teachings of true science and the declamations of misguided, though well-meaning, enthusiasts. They did what they believed to be right; and when roused to a sense of the greatness of their mistake, they did their very best to repair it, so that their city is said to be now the best vaccinated in Her Majesty's dominions. But though by their praiseworthy exertions they succeeded in promptly checking the raging epidemic, they cannot recall the dead to life, or restore beauty to marred features, or sight to blinded eyes. Would that the entire country and our Legislature might take duly to heat this object-lesson !

How completely the medical profession were convinced of the efficacy of vaccination in the early part of this century was strikingly illustrated by an account given by Professor Crookshank, in his interesting history of this subject, of several eminent medical men in Edinburgh meeting to see the—to them—unprecedented fact of a vaccinated person having taken smallpox. It has, of course, since become well known that the milder form of the disease, as modified by passing through the cow, confers a less permanent protection than the original human disorder. This it was, of course, impossible for Jenner to foresee. It is, indeed, a question of degree, since a second attack of ordinary smallpox is occasionally known to occur, and vaccination, long after it has ceased to give perfect immunity, greatly modifies the character of the disorder and diminishes its danger. And, happily, in re-vaccination after a certain number of years we have the means of making Jenner's work complete. I understand that the majority of the Commissioners, who have recently issued their report upon this subject, while recognising the value and importance of re-vaccination, are so impressed with the difficulties that would attend making it compulsory by legislation that they do not recommend that course; although it is advocated by two of their number who are of peculiarly high authority on such a question. I was lately told by a Berlin professor that no serious difficulty is experienced in carrying out the compulsory law that prevails in Germany. The masters of the schools are directed to ascertain in the case of every child attaining the age of twelve whether re-vaccination has been practised. If not, and the parents refuse to have it done, they are fined one mark. If this does not prove effectual, the fine is doubled; and if even the double penalty should not prove efficacious, a second doubling of it would follow, but, as my informant remarked, it is very seldom that it is called for. The result is that smallpox is a matter of extreme rarity in that country; while it is absolutely unknown in the huge German army, in consequence of the rule that every soldier is re-vaccinated on entering the service. Whatever view our Legislature may take on this question, one thing seems to me clear,—that it will be the duty of Government to encourage by every available means the use of calf lymph, so as to exclude the possibility of the communication of any human disease to the child, and to institute such efficient inspection of vaccination institutes as shall ensure careful antiseptic arrangements, and so prevent contamination by extraneous microbes. If this were done, "conscientious objections" would cease to have any rational basis. At the same time, the administration of the regulations on vaccination should be transferred (as advised by the Commissioners) to competent sanitary authorities.

But to return to Pasteur. In 1880 he entered upon the study of that terrible but then most obscure disease, Hydrophobia or Rabies, which from its infective character he was sure must be of microbic origin, although no micro-organism could be detected in it. He early demonstrated the new pathological fact that the virus had its essential seat in the nervous system. This proved the key to his success in this subject. One result that flowed from it has been the cause of unspeakable consolation to many. The foolish practice is still too prevalent of killing the dog that has bitten any one, on the absurd notion, that if it were mad, its destruction would prevent

the occurrence of hydrophobia in the person bitten. The idea of the bare possibility of the animal having been so affected causes an agony of suspense during the long weeks or months of possible incubation of the disease. Very serious nervous symptoms aping true hydrophobia have been known to result from the terror thus inspired. Pasteur showed that if a little of the brain or spinal cord of a dog that had been really mad was inoculated in an appropriate manner into a rabbit, it infallibly caused rabies in that animal in a few days. If therefore such an experiment was made with a negative result, the conclusion might be drawn with certainty that the dog had been healthy. It is perhaps right that I should say that the inoculation is painlessly done under an anæsthetic, and that in the rabbit rabies does not assume the violent form that it does in the dog, but produces gradual loss of power with little if any suffering.

This is the more satisfactory because rabbits in which the disease has been thus artifically induced are employed in carrying out what was Pasteur's greatest triumph,—the preventive treatment of hydrophobia in the human subject. We have seen that Pasteur discovered that microbes might under some circumstances undergo mitigation of their virulence. He afterwards found that under different conditions they might have it exalted, or, as he expressed it, there might be a *renforcement du virus*. Such proved to be the case with rabies in the rabbit; so that the spinal cords of animals which had died of it contained the poison in a highly intensified condition. But he also found that if such a highly virulent cord was suspended under strict antiseptic precautions in a dry atmosphere at a certain temperature, it gradually from day to day lost in potency, till in course of time it became absolutely inert. If now an emulsion of such a harmless cord was introduced under the skin of an animal, as in the subcutaneous administration of morphia, it might be followed without harm another day by a similar dose of a cord still rather poisonous; and so from day to day stronger and stronger injections might be used, the system becoming gradually accustomed to the poison, till a degree of virulence had been reached far exceeding that of the bite of a mad dog. When this had been attained, the animal proved incapable of taking the disease in the ordinary way; and more than that, if such treatment was adopted after an animal had already received the poison, provided that too long a time had not elapsed, the outbreak of the disease was prevented. It was only after great searching of heart that Pasteur, after consultation with some trusted medical friends, ventured upon trying this practice upon man. It has since been extensively adopted in various parts of the world with increasing success as the details of the method were improved. It is not of course the case that every one bitten by a really rabid animal takes the disease; but the percentage of those who do so, which was formerly large, has been reduced almost to zero by this treatment, if not too long delayed.

While the intensity of rabies in the rabbit is undoubtedly due to a peculiarly virulent form of the microbe concerned, we cannot suppose that the daily diminishing potency of the cord suspended in dry warm air is an instance of attenuation of virus, using the term "virus" as synonymous with the microbe concerned. In other words, we have no reason to believe that the special micro-organism of hydrophobia continues to develop in the dead cord and produce successively a milder and milder progeny, since rabies cannot be cultivated in the nervous system of a dead animal. We must rather conclude that there must be some chemical poison present which gradually loses its potency as time passes. And this leads me to refer to another most important branch of this large subject of bacteriology,—that of the poisonous products of microbes.

It was shown several years ago, by Roux and Yersin, working in the *Institut Pasteur*, that the crust or false membrane which forms upon the throats of patients affected with diphtheria contains bacteria which can be cultivated outside the body in a nutrient liquid, with the result that it acquires poisonous qualities of astonishing intensity, comparable to that of the secretion of the poison-glands of the most venomous serpents. And they also ascertained that the liquid retained this property after the microbes had been removed from it by filtration, which proved that the poison must be a chemical substance in solution, as distinguished from the living element which had produced it. These poisonous products of bacteria, or toxins as they have been termed, explain the deadly effects of some microbes, which it would otherwise be impossible to understand. Thus, in diphtheria itself the special bacillus which was shown by Löffler to be its cause, does not become propagated in the blood, like the microbe of chicken cholera, but remains confined to the surface on which it first appeared; but the toxin which it secretes is absorbed from that surface into the blood, and so poisons the system. Similar observations have been made with regard to the microbes of some other diseases, as, for example, the bacillus of tetanus or lockjaw. This remains localised in the wound, but forms a special toxin of extreme potency, which becomes absorbed and diffused through the body.

Wonderful as it seems, each poisonous microbe appears to form its own peculiar toxin. Koch's tuberculin was of this nature, a product of the growth of the tubercle bacillus in culture media. Here, again, great effects were produced by extremely minute quantities of the substance, but here a new peculiarity showed itself, viz., that patients affected with tubercular disease, in any of its varied forms, exhibited inflammation in the affected part and general fever after receiving under the skin an amount of the material which had no effect whatever upon healthy persons. I witnessed in Berlin some instances of these effects. which were simply astounding. Patients affected with a peculiar form of obstinate ulcer of the face showed, after a single injection of the tuberculin, violent inflammatory redness and swelling of the sore and surrounding skin; and, what was equally surprising, when this disturbance subsided the disease was found to have undergone great improvement. By repetitions of such procedures, ulcers which had previously been steadily advancing, in spite of ordinary treatment, became greatly reduced in size, and in some instances apparently cured. Such results led Koch to believe that he had obtained an effectual means of dealing with tubercular disease in all its forms. Unhappily, the apparent cure proved to be only of transient duration, and the high hopes which had been inspired by Koch's great reputation were dashed. It is but fair to say that he was strongly urged to publish before he was himself disposed to do so, and we cannot but regret that he yielded to the pressure put upon him.

But though Koch's sanguine anticipations were not realised, it would be a great mistake to suppose that his labours with tuberculin have been fruitless. Cattle are liable to tubercle, and, when affected with it, may become a very serious source of infection for human beings, more especially when the disease affects the udders of cows, and so contaminates the milk. By virtue of the close affinity that prevails between the lower animals and ourselves, in disease as well as in health, tuberculin produces fever in tubercular cows in doses which do not affect healthy beasts. Thus, by the subcutaneous use of a little of the fluid, tubercle latent in internal organs of an apparently healthy cow can be with certainty revealed, and the slaughter of the animal after this discovery protects man from infection.

It has been ascertained that glanders presents a precise analogy with tubercle as regards the effects of its toxic products. If the microbe which has been found to be the cause of this disease is cultivated in appropriate media, it produces a poison which has received the name of mallein, and the subcutaneous injection of a suitable dose of this fluid into a glandered horse causes striking febrile symptoms which do not occur in a healthy animal. Glanders, like tubercle, may exist in insidious latent

forms which there was formerly no means of detecting, but which are at once disclosed by this means. If a glandered horse has been accidentally introduced into a large stable, this method of diagnosis surely tells if it has infected others. All receive a little mallein. Those which become affected with fever are slaughtered, and thus not only is the disease prevented from spreading to other horses, but the grooms are protected from a mortal disorder.

This valuable resource sprang from Koch's work on tuberculin, which has also indirectly done good in other ways. His distinguished pupil, Behring, has expressly attributed to those researches the inspiration of the work which led him and his since famous collaborateur, the Japanese Kitasato, to their surprising discovery of anti-toxic serum. They found that if an animal of a species liable to diphtheria or tetanus received a quantity of the respective toxin so small as to be harmless, and afterwards, at suitable intervals, successively stronger and stronger doses, the creature, in course of time, acquired such a tolerance for the poison as to be able to receive with impunity a quantity very much greater than would at the outset have proved fatal. So far, we have nothing more than seems to correspond with the effects of the increasingly potent cords in Pasteur's treatment of rabies. But what was entirely new in their results was that, if blood was drawn from an animal which had acquired this high degree of artifical immunity, and some of the clear fluid or serum which exuded from it after it had clotted was introduced under the skin of another animal, this second animal acquired a strong, though more transient, immunity against the particular toxin concerned. The serum in some way counteracted the toxin, or was anti-toxic. But, more than that, if some of the anti-toxic serum was applied to an animal after it had already received a poisonous dose of the toxin, it preserved the life of the creature, provided that too long a time had not elapsed after the poison was introduced. In other words, the antitoxin proved to be not only preventive but curative.

Similar results were afterwards obtained by Ehrlich, of Berlin, with some poisons not of bacterial origin, but derived from the vegetable kingdom; and quite recently the independent labours of Calmette of Lille and Fraser of Edinburgh have shown that antidotes of wonderful efficacy against the venom of serpents may be procured on the same principle. Calmette has otained anti-toxin so powerful that a quantity of it only a 200,000th part of the weight of an animal will protect it perfectly against a dose of the secretion of the poison-glands of the most venomous serpents known to exist, which without such protection would have proved fatal in four hours. For curative purposes larger quantities of the remedy are required, but cases have been already published by Calmette in which death appears to have been averted in the human subject by this treatment.

Behring's darling object was to discover means of curing tetanus and diphtheria in man. In tetanus the conditions are not favourable; because the specific bacilli lurk in the depths of the wound, and only declare their presence by symptoms caused by their toxin having been already in a greater or less amount diffused through the system; and in every case of this disease there must be a fear that the antidote may be applied too late to be useful. But in diphtheria the bacilli very early manifest their presence by the false membrane which they cause upon the throat, so that the anti-toxin has a fair chance; and here we are justified in saying that Behring's object has been attained.

The problem, however, was by no means so simple as in the case of some mere chemical poison. However effectual the anti-toxin might be against the toxin, if it left the bacilli intact, not only would repeated injections be required to maintain the transient immunity to the poison perpetually secreted by the microbes, but the bacilli might by their growth and extension cause obstruction of the respiratory passages.

Roux, however, whose name must always be mentioned with honour in relation to this subject, effectually disposed of this difficulty. He showed by experiments on animals that a diphtheritic false membrane, rapidly extending and accompanied by surrounding inflammation, was brought to a stand by the use of the anti-toxin, and soon dropped off, leaving a healthy surface. Whatever be the explanation, the fact was thus established that the anti-toxic serum, while it renders the toxin harmless, causes the microbe to languish and disappear.

No theoretical objection could now be urged against the treatment; and it has during the last two years been extensively tested in practice in various parts of the world, and it has gradually made its way more and more into the confidence of the profession. One important piece of evidence in its favour in this country is derived from the report of the six large hospitals under the management of the London Asylums Board. The medical officers of these hospitals at first naturally regarded the practice with scepticism; but as it appeared to be at least harmless, they gave it a trial, and during the year 1895 it was very generally employed upon the 2182 cases admitted, and they have all become convinced of its great value. In the nature of things, if the theory of the treatment is correct, the best results must be obtained when the patients are admitted at an early stage of the attack, before there has been time for much poisoning of the system; and accordingly we learn from the Report that, comparing 1895 with 1894, during which latter year the ordinary treatment had been used, the percentage of mortality, in all the six hospitals combined, among the patients admitted on the first day of the disease, which in 1894 was 22·5, was only 4·6 in 1895; while for those admitted on the second day the numbers are 27 for 1894 and 14·8 for 1895. Thus for cases admitted on the first day the mortality was only one-fifth of what it was in the previous year, and for those entering on the second it was halved. Unfortunately in the low parts of London which furnish most of these patients the parents too often delay sending in the children till much later; so that on the average no less than 67·5 per cent were admitted on the fourth day of the disease or later. Hence the aggregate statistics of all cases are not nearly so striking. Nevertheless, taking it altogether, the mortality in 1895 was less than had ever before been experienced in those hospitals. I should add that there was no reason to think that the disease was of a milder type than usual in 1895, and no change whatever was made in the treatment except as regards the anti-toxic injections.

There is one piece of evidence recorded in the report which, though it is not concerned with high numbers, is well worthy of notice. It relates to a special institution to which convalescents from scarlet fever are sent from all the six hospitals. Such patients occasionally contract diphtheria, and when they do so the added disease has generally proved extremely fatal. In the five years preceding the introduction of the treatment with anti-toxin the mortality from this cause had never been less than 50 per cent, and averaged on the whole 61·9 per cent. During 1895, under anti-toxin, the deaths among the 119 patients of this class were only 7·5 per cent, or one-eighth of what had been previously experienced. This very striking result seems to be naturally explained by the fact that these patients being already in hospital when the diphtheria appeared, an unusually early opportunity was afforded for dealing with it.

There are certain cases of so malignant a character from the first that no treatment will probably ever be able to cope with them. But taking all cases together it seems probable that Behring's hope that the mortality may be reduced to 5 per cent will be fully realised when the public become alive to the paramount importance of having the treatment commenced at the outset of the disease.

There are many able workers in the field of Bacteriology whose names time does not permit me to mention, and to whose important labours I cannot refer; and even those researches of which I have spoken have been, of course, most inadequately dealt with. I feel this especially with regard to Pasteur, whose work shines out more brightly the more his writings are perused.

I have lastly to bring before you a subject which, though not bacteriological, has intimate relations with bacteria. If a drop of blood is drawn from the finger by a prick with a needle, and examined microscopically between two plates of glass, there are seen in it minute solid elements of two kinds, the one pale orange bi-concave discs, which, seen in mass, give the red colour to the vital fluid, the other more or less granular spherical masses of the soft material called protoplasm, destitute of colour, and therefore called the colourless or white corpuscles. It has been long known that if the microscope was placed at such a distance from a fire as to have the temperature of the human body, the white corpuscles might be seen to put out and retract little processes or pseudopodia, and by their means crawl over the surface of the glass, just like the extremely low forms of animal life termed—from this faculty of changing their form—amœbæ. It was a somewhat weird spectacle, that of seeing what had just before been constituents of our own blood moving about like independent creatures. Yet there was nothing in this inconsistent with what we knew of the fixed components of the animal frame. For example, the surface of a frog's tongue is covered with a layer of cells, each of which is provided with two or more lashing filaments or cilia, and those of all the cells acting in concert cause a constant flow of fluid in a definite direction over the organ. If we gently scrape the surface of the animal's tongue, we can detach some of these ciliated cells; and on examining them with the microscope in a drop of water we find that they will continue for an indefinite time their lashing movements, which are just as much living or vital in their character as the writhings of a worm. And, as I observed many years ago, these detached cells behave under the influence of a stimulus just like parts connected with the body, the movements of the cilia being excited to greater activity by gentle stimulation, and thrown into a state of temporary inactivity when the irritation was more severe. Thus each constituent element of our bodies may be regarded as in one sense an independent living being, though all work together in marvellous harmony for the good of the body politic. The independent movements of the white corpuscles outside the body were therefore not astonishing; but they long remained matters of mere curiosity. Much interest was called to them by the observations of the German pathologist Cohnheim, that in some inflammatory conditions they passed through the pores in the walls of the finest blood-vessels, and thus escaped into the interstices of the surrounding tissues. Cohnheim attributed their transit to the pressure of the blood. But why it was that, though larger than the red corpuscles, and containing a nucleus which the red ones have not, they alone passed through the pores of the vessels, or why it was that this emigration of the white corpuscles occurred abundantly in some inflammations and was absent in others, was quite unexplained.

These white corpuscles, however, have been invested with extraordinary new interest by the researches of the Russian naturalist and pathologist, Metchnikoff. He observed that, after passing through the walls of the vessels, they not only crawl about like amœbæ, but, like them, receive nutritious materials into their soft bodies and digest them. It is thus that the effete materials of a tadpole's tail are got rid of, so that they play a most important part in the function of absorption.

But still more interesting observations followed. He found that a microscopic crustacean, a kind of water-flea, was liable to be infested by a fungus which had exceedingly sharp-pointed spores. These were apt to penetrate the coats of the creature's intestine, and project into its body-cavity. No sooner did this occur with any spore than it became surrounded with a group of the cells which are contained in the cavity of the body and correspond to the white corpuscles of our blood. These proceeded to attempt to devour the spore; and if they succeeded, in every such case the animal was saved from the invasion of the parasite. But if the spores were more than could be disposed of by the devouring cells (phagocytes, as Metchnikoff termed them), the water-flea succumbed.

Starting from this fundamental observation, he ascertained that the microbes of infective diseases are subject to this same process of devouring and digestion, carried on both by the white corpuscles and by cells that line the blood-vessels. And by a long series of most beautiful researches he has, as it appears to me, firmly established the great truth that phagocytosis is the main defensive means possessed by the living body against the invasions of its microscopic foes. The power of the system to produce anti-toxic substances to counteract the poisons of microbes is undoubtedly in its own place of great importance. But in the large class of cases in which animals are naturally refractory to particular infective diseases the blood is not found to yield any anti-toxic element by which the natural immunity can be accounted for. Here phagocytosis seems to be the sole defensive agency. And even in cases in which the serum does possess anti-toxic, or, as it would seem in some cases, germicidal properties, the bodies of the dead microbes must at last be got rid of by phagocytosis, and some recent observations would seem to indicate that the useful elements of the serum may be, in part at least, derived from the digestive juices of the phagocytes. If ever there was a romantic chapter in pathology, it has surely been that of the story of phagocytosis.

I was myself peculiarly interested by these observations of Metchnikoff's, because they seemed to me to afford clear explanation of the healing of wounds by first intention under circumstances before incomprehensible. This primary union was sometimes seen to take place in wounds treated with water-dressing; that is to say, a piece of wet lint covered with a layer of oiled silk to keep it moist. This, though cleanly, when applied, was invariably putrid within twenty-four hours. The layer of blood between the cut surfaces was thus exposed at the outlet of the wound to a most potent septic focus. How was it prevented from putrefying, as it would have done under such influence if, instead of being between divided living tissues, it had been between plates of glass or other indifferent material? Pasteur's observations pushed the question a step further. It now was, How were the bacteria of putrefaction kept from propagating in the decomposable film? Metchnikoff's phagocytosis supplied the answer. The blood between the lips of the wound became rapidly peopled with phagocytes, which kept guard against the putrefactive microbes and seized them as they endeavoured to enter.

If phagocytosis was ever able to cope with septic microbes in so concentrated and intense a form, it could hardly fail to deal effectually with them in the very mitigated condition in which they are present in the air. We are thus strongly confirmed in our conclusion that the atmospheric dust may be safely disregarded in our operations: and Metchnikoff's researches, while they have illumined the whole pathology of infective diseases, have beautifully completed the theory of antiseptic treatment in surgery.

I might have taken equally striking illustrations of my theme from other departments in which microbes play no part. In fact, any attempt to speak of all that the art of healing has borrowed from science and contributed to it during the past half-century would involve a very extensive dissertation on pathology and therapeutics. I have culled specimens from a wide field; and I only hope that in bringing them before you I have not overstepped the bounds of what is fitting before a mixed company. For

many of you my remarks can have had little if any novelty : for others they may perhaps possess some interest as showing that Medicine is no unworthy ally of the British Association—that, while her practice is ever more and more based on science, the ceaseless efforts of her votaries to improve what have been fittingly designated *Quæ prosunt omnibus artes*, are ever adding largely to the sum of abstract knowledge.

# ADDRESS TO THE CHEMICAL SECTION
## OF THE
### BRITISH ASSOCIATION.
#### LIVERPOOL, 1896.

By Dr. LUDWIG MOND, F.R.S., President of the Section.

IN endeavouring to fix upon a suitable theme for the address I knew you would to-day expect from me, I have felt that I ought to give due consideration to the interests which tie this magnificent city of Liverpool, whose hospitality we enjoy this week, to Section B of the British Association.

I have therefore chosen to give you a brief history of the manufacture of chlorine, with the progress of which this city and its neighbourhood have been very conspicuously and very honourably connected, not only as regards quantity —I believe this neighbourhood produces to-day nearly as much chlorine as the rest of this world together—but more particularly by having originated, worked out, and carried into practice several of the most important improvements ever introduced into this manufacture. I was confirmed in my choice by the fact that this manufacture has been influenced and perfected in an extraordinary degree by the rapid assimilation and application of the results of purely scientific investigations and of new scientific theories, and offers a very remarkable example of the incalculable value to our commercial interests of the progress of pure science.

The early history of chlorine is particularly interesting, as it played a most important *rôle* in the development of chemical theories. There can be no doubt that the Arabian alchemist Geber, who lived eleven hundred years ago, must have known that "Aqua Regia," which he prepared by distilling a mixture of salt, nitre, and vitriol, gave off on heating very corrosive, evil-smelling, greenish yellow fumes, and all his followers throughout a thousand years must have been more or less molested by these fumes whenever they used aqua regia, the one solvent of the gold they attempted so persistently to produce.

But it was not until 1774 that the great Swedish chemist Scheele succeeding in establishing the character of these fumes. He discovered that on heating manganese with muriatic acid he obtained fumes very similar to those given off by "aqua regia," and found that these fumes constituted a permanent gas of yellowish green colour, very pungent odour, very corrosive, very irritating to the respiratory organs, and which had the power of destroying organic colouring-matters.

According to the views prevalent at the time, Scheele considered that the manganese had removed phlogiston from the muriatic acid, and he consequently called the gas dephlogisticated muriatic acid.

When during the next decade Lavoisier successfully attacked, and after a memorable struggle completely upset, the phlogiston theory and laid the foundations of our modern chemistry, Berthollet, the eminent "father" of physical chemistry—the science of to-day—endeavoured to determine the place of Scheele's gas in the new theory. Lavoisier was of opinion that all acids, including muriatic acid, contain oxygen. Berthollet found that a solution of Scheele's gas in water, when exposed to the sunlight, gives off oxygen and leaves behind muriatic acid. He considered this as proof that this gas consists of muriatic acid and oxygen, and called it oxygenated muriatic acid.

In the year 1785 Berthollet conceived the idea of utilising the colour destroying powers of this gas for bleaching purposes. He prepared the gas by heating a mixture of salt, manganese, and vitriol. He used a solution of the gas in water for bleaching, and subsequently discovered that the product obtained by absorbing the gas in a solution of caustic potash possessed great advantages in practice.

This solution was prepared as early as 1789, at the chemical works on the Quai de Javelle, in Paris, and is still made and used there under the name of "Eau de Javelle."

James Watt, whose great mind was not entirely taken up with that greatest of all inventions—his steam engine —by which he has benefitted the human race more than any other man, but who also did excellent work in chemistry—became acquainted in Paris with Berthollet's process, and brought it to Scotland. Here it was taken up with that energy characteristic of the Scotch, and a great stride forward was made when, in 1798, Charles Tennant, the founder of the great firm which has only recently lapsed into the United Alkali Company, began to use milk of lime in place of the more costly caustic potash, in making a bleaching liquid ; and a still greater advance was made when, in the following year, Tennant proposed to absorb the chlorine by hydrate of lime, and thus to produce a dry substance, since known under the name of bleaching-powder, which allowed the bleaching powers of chlorine to be transported to any distance.

In order to give you a conception of the theoretical ideas prevalent at this time, I will read to you a passage from an interesting treatise on the art of bleaching published in 1799 by Higgins. In his chapter "On Bleaching with the Oxygenated Muriatic Acid, and on the Methods of Preparing it," he explains the theory of the process as follows :—

"Manganese is an oxyd, a metal saturated with oxygen gas. Common salt is composed of muriatic acid and an alkaline salt called soda, the same which barilla affords. Manganese has greater affinity to sulphuric acid than to its oxygen, and the soda of the salt greater affinity to sulphuric acid than to the muriatic acid gas ; hence it necessarily follows that these two gases (or rather their gravitating matter) must be liberated from their former union in immediate contact with each other ; and although they have but a weak affinity to one another, they unite in their nascent state, that is to say, before they individually unite to caloric, and separately assume the gaseous state ; for oxygen gas and muriatic acid gas already formed will not unite when mixed, in consequence principally of the distance at which their respective atmospheres of caloric keep their gravitating particles asunder. The compound resulting from these two gases still retains the property of assuming the gaseous state, and is the oxygenated muriatic gas."

Interesting as these views may appear, considering the time they were published, you will notice that the *rôle* played by the manganese in the process and the chemical nature of this substance were not at all understood. the law of multiple proportions had not yet been propounded by John Dalton, and the researches of Berzelius on the oxides of manganese were only published thirteen years later, in 1812. The green gas we are considering was still looked upon as muriatic acid to which oxygen had been added, in contradistinction to Scheele's view, who considered it as muriatic acid from which something, viz., phlogiston, had been abstracted.

It was Humphry Davy who had, by a series of brilliant investigations carried out in the Laboratory of the Royal Institution between 1808 and 1810, accumulated fact upon fact to prove that the gas hitherto called oxygenated muriatic acid did not contain oxygen. He announced in an historic paper, which he read before the Royal Society on July 12, 1810, his conclusion that this gas was an elementary body, which in muriatic acid was combined with hydrogen, and for which he proposed the name "chlorine,"

derived from the Greek χλωρός, signifying "green," the colour by which the gas is distinguished.

The numerous communications which Humphry Davy made to the Royal Society on this subject form one of the brightest and most interesting chapters in the history of chemistry. They have recently been reprinted by the Alembic Society, and I cannot too highly recommend their study to the young students of our science.

Those who have followed the history of chemistry I need not remind how hotly and persistently Davy's views were combated by a number of the most eminent chemists of his time, led by Berzelius himself; how long the chlorine controversy divided the chemical world; how triumphantly Davy emerged from it; how completely his views were recognised; and how very instrumental they have been in advancing theoretical chemistry.

The hope, however, which Davy expressed in that same historic paper, "that these new views would perhaps facilitate one of the greatest problems in economical chemistry, the decomposition of the muriates of soda and potash," was not to be realised so soon. Although it had changed its name, chlorine was still for many years manufactured by heating a mixture of salt, manganese, and sulphuric acid in leaden stills, as before.

This process leaves a residue consisting of sulphate of soda and sulphate of manganese, and for some time attempts were made to recover the sulphate of soda from these residues, and to use it for the manufacture of carbonate of soda by the Le Blanc process. On the other hand, the Le Blanc process, which had been discovered and put into practice almost simultaneously with Berthollet's chlorine process, decomposed salt by sulphuric acid, and sent the muriatic acid evolved into the atmosphere, causing a great nuisance to the neighbourhood.

Naturally, therefore, when Mr. William Gossage had succeeded in devising plant for condensing this muriatic acid, the manufacturers of chlorine reverted to the original process of Scheele, and heated manganese with the muriatic acid thus obtained. Since then the manufacture of chlorine has become a by-product of the manufacture of soda by the Le Blanc process, and remained so till very recently.

For a great many years the muriatic acid was allowed to act upon native ores of manganese in closed vessels of earthenware or stone, to which heat could be applied, either externally or internally. These native manganese ores, containing only a certain amount of peroxide, converted only a certain percentage of the muriatic acid employed into free chlorine, the rest combining with the manganese and iron contained in the ore, and forming a brown and very acid solution, which it was a great difficulty for the manufacturer to get rid of. Consequently, many attempts were made to regenerate peroxide of manganese from these waste liquors, so as to use it over again in the production of chlorine.

These, however, for a long time remained unsuccessful, because the exact conditions for super-oxidising the protoxide of manganese by means of atmospheric air were not yet known.

Meantime, viz., in 1845, Mr. Dunlop introduced into the works created by his grandfather, Mr. Charles Tennant, at St. Rollox, a new and very interesting method for producing chlorine, which was in a certain measure a return to the process used by the alchemists.

Indeed, the first part of this process consisted in decomposing a mixture of salt and nitre with oil of vitriol—a reaction that had been made use of for so many centuries! The chlorine so obtained is, however, not pure, but a mixture of chlorine with oxides of nitrogen and hydrochloric acid, which Mr. Dunlop had to find means to eliminate.

For separating the nitrous oxides Mr. Dunlop adopted the method introduced twenty years before by the great Gay-Lussac, in connection with vitriol-making, viz., absorption by sulphuric acid, and the nitro-sulphuric acid

thus formed he also utilised in the same way as that obtained from the towers which still bear Gay-Lussac's illustrious name, viz., by using it in the vitriol process in lieu of nitric acid. He then freed his chlorine gas from hydrochloric acid by washing with water, and so obtained it pure. This process possessed two distinct advantages— (1) It yielded a very much larger amount of chlorine from the same amount of salt, and (2) the nitric acid, which was used for oxidising the hydrogen in the hydrochloric acid, was not lost, because the oxides of nitrogen to which it was reduced answered the purpose for which the acid itself had previously been employed. But this process was very limited in its application, as it could only be worked to the extent to which nitric acid was used in vitriol-making.

The process has been at work at St. Rollox for over fifty years, and, as far as I know, is there still in operation; but I am not aware that it has ever been taken up elsewhere.

Within the last few years, however, several serious attempts have been made to give this process a wider scope by re-generating nitric acid from the nitro-sulphuric acid and employing it over and over again to convert hydrochloric acid into chlorine. Quite a number of patents have been taken out for this purpose, all employing atmospheric air for re-converting the nitrous oxides into nitric acid, and differing mainly in details of apparatus and methods of work, and several of these have been put to practical test on a fairly large scale in this neighbourhood, and also in Glasgow, Middlesbrough, and elsewhere. As I do not want to keep you here the whole afternoon, I have to draw the line somewhere as to what I shall include in this brief history of the manufacture of chlorine, and have had to decide to restrict myself to those methods which have actually attained the rank of manufacturing processes on a large scale. As none of the processes just referred to have attained that position, you will excuse me for not entering into further details respecting them.

Mr. Dunlop's process only produced a very small portion of the chlorine manufactured at that time at St. Rollox, the remainder being made, as before, from native manganese and muriatic acid, leaving behind the very offensive waste liquors I have mentioned before, which increased from year to year, and became more and more difficult to get rid of. The problem of recovering from these liquors the manganese in the form of peroxide Mr. Dunlop succeeded in solving in 1855.

He neutralised the free acid and precipitated the iron present by treating these liquors with ground chalk in the cold and settling out, and in later years, filter-pressing the precipitate, which left him a solution of chloride of manganese, mixed only with chloride of calcium. This was treated with a fresh quantity of milk of chalk, but this time under pressure in closed vessels provided with agitators and heated by steam, under which conditions all the manganese was precipitated as carbonate of manganese. This precipitate was filtered off and well drained, and was then passed on iron trays mounted on carriages through long chambers, in which it was exposed to hot air at a temperature of 300° C., the process being practically made continuous, one tray at the one end being taken out of these chambers, and a fresh tray being put in at the other end. One passage through these chambers sufficed to convert the carbonate of manganese into peroxide, which was used in place of, and in the same way as, the native manganese.

The whole of the residual liquors made at the large works at St. Rollox have been treated by this process with signal success for a long number of years. For a short time the process was discontinued in favour of the Weldon process (of which I have to speak next); but after two years Dunlop's process was taken up again, and to the best of my knowledge it is still in operation to this day. It has, however, just like Mr. Dunlop's first chlorine process, never left the place of its birth (St.

Rollox), although it was for a period of over ten years without a rival.

In 1866 Mr. Walter Weldon patented a modification of a process proposed by Mr. William Gossage in 1837 for recovering the manganese that had been used in the manufacture of chlorine. Mr. Gossage had proposed to treat the residual liquors of this manufacture by lime, and to oxidise the resulting protoxide of manganese by bringing it into frequent and intimate contact with atmospheric air. This process—and several modifications thereof subsequently patented—had been tried in various places without success. Mr. Weldon, however, did succeed in obtaining a very satisfactory result, possibly—even probably—because, not being a chemist, he did not add the equivalent quantity of lime to his liquor to precipitate the manganese, but used an excess. However, Mr. Weldon, if he was not a chemist at that time, was a man of genius and of great perseverance. He soon made himself a chemist, and having once got a satisfactory result, he studied every small detail of the reaction with the utmost tenacity until he had thoroughly established how this satisfactory result could be obtained on the largest scale with the greatest regularity and certainty.

He even went further, and added considerably to our theoretical knowledge of the character of manganese peroxide and similar peroxides by putting forward the view that these compounds possess the character of weak acids. He explained in this way the necessity for the presence of an excess of lime or other base if the oxidation of the precipitated protoxide of manganese by means of atmospheric air was to proceed at a sufficiently rapid rate. He pointed out that the product had to be considered as a manganite of calcium, a view which has since been thoroughly proved by the investigations of Goergen and others; and it is only fair to state that Weldon's process is not only a process for recovering the peroxide of manganese originally used, but that he introduced a new substance, viz., manganite of calcium, to be continuously used over and over again in the manufacture of chlorine.

Mr. Weldon had the good fortune that his ideas were taken up with fervency by Colonel Gamble of St. Helen's, and that Colonel Gamble's manager, Mr. F. Bramwell, placed all his experience as a consummate technical chemist and engineer at Mr. Weldon's disposal, and assisted him in carrying his ideas into practice. The result was that a process which many able men had tried in vain to realise for thirty years became, in the hands of Mr. Weldon and his coadjutors, within a few years, one of the greatest successes achieved in manufacturing chemistry.

The Weldon process commences by treating the residual liquor with ground chalk or limestone, thus neutralising the free acid and precipitating any sulphuric acid and oxide of iron present. The clarified liquor is run into a tall cylindrical vessel, and milk of lime is added in sufficient quantity to precipitate all the manganese in the form of protoxide. An additional quantity of milk of lime, from one-fifth to one-third of the quantity previously used, is then introduced, and air passed through the vessel by means of an air-compressor. After a few hours all the manganese is converted into peroxide; the contents of the vessel are then run off; the mud, now everywhere known as "Weldon mud," is settled, and the clear liquor run to waste. The mud is then pumped into large closed stone stills, where it meets with muriatic acid, chlorine is given off, and the residual liquor treated as before.

You note that this process works without any manipulation, merely by the circulation of liquids and thick magmas which are moved by pumping machinery. As compared to older processes it also has the great advantage that it requires very little time for completing the cycle of operations, so that large quantities of chlorine can be produced by a very simple and inexpensive plant.

These advantages secured for this process the quite unprecedented success that within a few years it was adopted, with a few isolated exceptions, by every large manufacturer of chlorine in the world; yet it possessed a distinct drawback, viz., that it produced considerably less chlorine from a given quantity of muriatic acid than either native manganese of good quality or Mr. Dunlop's recovered manganese. At that time, however, muriatic acid was produced as a by-product of the Le Blanc process so largely in excess of what could be utilised that it was generally looked upon as a waste product of no value. Mr. Weldon himself was one of the very few who foresaw that this state of things could not always continue. The ammonia soda process was casting its shadow before it. Patented in 1838 by Messrs. Dyar and Hemming, it was only after the lapse of thirty years (during which a number of manufacturing chemists of the highest standing had in vain endeavoured to carry it into practice) that this process was raised to the rank of a manufacturing process, through the indomitable perseverance of Mr. Ernest Solvay of Brussels, and his clear perception of its practical and theoretical intricacies. A few years later, in 1872, Mr. Weldon already gave his attention to the problem of obtaining the chlorine of the salt used in this process in the form of muriatic acid. He proposed to recover the ammonia from the ammonium chloride obtained in this manufacture by magnesia instead of lime, thus obtaining magnesium chloride instead of calcium chloride, and to produce muriatic acid from this magnesium chloride by a process patented by Clemm in 1863, viz., by evaporating the solution, heating the residue in the presence of steam, and condensing the acid vapours given off.

Strange to say, this same method had been patented by Mr. Ernest Solvay within twenty-four hours before Mr. Weldon lodged his specification. It has been frequently tried with many modifications, but has never been found practicable. Soon afterwards Mr. Weldon, with the object of reducing the muriatic acid required by his first process, proposed to replace the lime in this process by magnesia, and so to produce a manganite of magnesia. After treating this with muriatic acid and liberating chlorine, he proceeded to evaporate the residual liquors to dryness, during which operation all the chlorine they contain would be disengaged as hydrochloric acid and collected in condensers, while the dry residue, after being heated to dull redness in the presence of air, would be reconverted into manganite of magnesia.

This process was made the subject of long and extensive experiments at the works of Messrs. Gamble at St. Helens, but did not realise Mr. Weldon's expectations. It, however, led to some further interesting developments, to which I shall refer later on.

Those of you who were present at the last meeting of the British Association in this city will remember that this Section had the advantage of listening to a paper by Mr. Weldon on his chlorine process, and also to another highly interesting paper by Mr. Henry Deacon of Widnes, "On a New Chlorine Process without Manganese." And those of you who came with the then President of the Section (Professor Roscoe) to Widnes, to visit the works of Messrs. Gaskell, Deacon, and Co., will well remember that at these works they saw, side by side, Weldon's process and Deacon's process in operation, and no one present will have forgotten the thoughtful flashing eyes and impressive face of Mr. Deacon when he explained to his visitors the theoretical views he had formed as regards his process.

Mr. Deacon had made a careful study of thermo-chemistry, which had been greatly developed during the preceding decade by the painstaking, accurate, and comprehensive experiments of Julius Thomsen and of Berthelot, and had led the latter to generalisations, which, although not fully accepted by scientific men, have been of immense service to manufacturing chemistry.

## LUCIUM, A NEW ELEMENT.

IN the course of researches on monazite sand M. P. Barrière appears to have come upon a new elementary body, to which he has given the name *Lucium*, and which he purposes using for the production of an incandescent gas light in opposition to that of Auer von Welsbach.

Hence he has sought to show the new and independent character of lucium in order to prove that its use was not anticipated by the Welsbach patents. A careful examination led to the following results.

The chemical properties of lucium are as follows :—The salts of cerium, lanthanum, and didymium form with sodium sulphate insoluble double salts ; lucium does not. Thorium and zirconium form insoluble double salts with potassium sulphate ; this is not the case with lucium. Yttrium, ytterbium, and erbium are not precipitable by sodium thiosulphate, whilst lucium chloride is precipitable. From glucinium lucium differs, as its salts are precipitable by oxalic acid.

According to the results obtained by Prof. Schützenberger, confirmed by those of Cleve, Fresenius, and Lecoq de Boisbaudran, lucium dissolves in sulphuric, nitric, or acetic acid, forming salts either white or slightly tinted with rose-colour. All its salts are soluble in water, forming limpid, colourless solutions.

The spectral rays of lucium are special, and only approximate slightly to those of erbium. Erbium oxide, on ignition, appears of a very pure rose-colour, and its nitrate is red. On the contrary, lucium oxide is white, slightly greyish, and its nitrate is white. The aqueous solutions of the erbium salts are red or rose-colour ; those of lucium, even if containing 15 or 20 per cent of the salt, are almost colourless.

The atomic weight of lucium is calculated as = 104, whilst—

| | |
|---|---|
| Thorium | = 233 |
| Yttrium | = 89 |
| Ytterbium | = 173 |
| Scandium | = 44·5 |
| Cerium | = 140 |
| Lanthanum | = 156 |
| Erbium | = 166 |
| Zirconium | = 90 |
| Samarium | = 150 |
| Glucinium | = 9 |

Hence the authorities cited regard lucium as a new, distinct elementary body.

## THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.[*]

By the Baron HANNS JÜPTNER VON JONSTORFF
(Neuberg, Austria).

8. *The want of homogeneity of the sample* is one of the most important sources of error. It deserves most special attention in any case where it is a question of exhaustively testing analytical methods, since it is only when there is absolute certainty of the actual homogeneous composition of the material used in the parallel analyses that it is possible to obtain a trustworthy judgment upon the methods used.

This want of homogeneity of the sample is met with, however, in various ways. It is mostly shown in the varying composition of an ingot at the base or at the top, externally or internally. These are liquation phenomena, the results of which are very clearly shown in the following results of investigations by Snelus. From an ingot mea-

suring 19 by 19 by 84 inches, which was allowed to cool extremely slowly, he cut sections 4 inches above the base and 21 inches below the top, perpendicular to the axis, and from each of these sections he took six samples, No. 1 being at the corner, and No. 6 at the centre of the plate. The analyses gave the following results :—

| No. | Top Plate. | | | Base Plate. | | |
|---|---|---|---|---|---|---|
| | Carbon. | Silicon. | Phosphorus. | Carbon. | Silicon. | Phosph. |
| 1 | 0·44 | 0·032 | 0·044 | 0·44 | 0·048 | 0·060 |
| 2 | 0·54 | 0·048 | 0·060 | 0·42 | 0·058 | 0·062 |
| 3 | 0·57 | 0·080 | 0·086 | 0·41 | 0·048 | 0·054 |
| 4 | 0·61 | 0·096 | 0·097 | 0·40 | 0·048 | 0·048 |
| 5 | 0·68 | 0·120 | 0·111 | 0·38 | 0·048 | 0·058 |
| 6 | 0·77 | 0·187 | 0·142 | 0·37 | 0·048 | 0·052 |

This want of homogeneity must obviously, also, be met with in the products obtained by cutting or rolling such ingots. Thus Eccles found that soft plates, of which the fracture at the two exterior sides was silky and in the centre granular, had the following composition :—

| | Granular layer. Per cent. | Silky portion. Per cent. |
|---|---|---|
| Carbon .. .. .. | 0·160 | 0·115 |
| Phosphorus .. .. | 0·112 | 0·038 |
| Sulphur .. .. .. | 0·070 | 0·030 |
| Manganese .. .. | 0·570 | 0·576 |

A sheet 30 millimetres thick had the following composition :—

| | Carbon. | Sulphur. | Phosphorus. | Manganese. |
|---|---|---|---|---|
| *Top End.* | | | | |
| Exterior :— | | | | |
| Longitudinal section | 0·240 | 0·025 | 0·050 | 0·160 |
| Cross section .. .. | 0·240 | 0·017 | 0·052 | 0·150 |
| Interior :— | | | | |
| Longitudinal section | 0·320 | 0·061 | 0·100 | 0·088 |
| Cross section .. .. | 0·400 | 0·070 | 0·088 | 0·140 |
| *Bottom End.* | | | | |
| Exterior :— | | | | |
| Longitudinal section | 0·250 | 0·028 | 0·060 | 0·120 |
| Cross section .. .. | 0·250 | 0·030 | 0·070 | 0·110 |
| Interior :— | | | | |
| Longitudinal section | 0·250 | 0·022 | 0·060 | 0·120 |
| Cross section .. .. | 0·200 | 0·031 | 0·052 | 0·120 |

A. R. von Dormus (*Zeitschr. des Oesterr. Ing.inieur und Architekten Vereins,* 1896, Nos. 13, 14, 15) gives the following interesting analyses of steel rails :—

| No. | Point at which sample was taken. | C. | Si. | Mn. | P. | S. | Co. |
|---|---|---|---|---|---|---|---|
| 358 | Surface.. .. | 0·411 | 0·011 | 0·477 | 0·063 | 0·026 | 0·130 |
| ,, | Centre of head | 0·525 | 0·007 | 0·506 | 0·104 | 0·038 | 0·126 |
| ,, | Neck .. .. | 0·485 | 0·010 | 0·506 | 0·099 | 0·040 | 0·123 |
| ,, | Base .. .. | 0·456 | 0·009 | 0·488 | 0·064 | 0·025 | 0·109 |
| 4185 | Surface.. .. | 0·396 | 0·013 | 0·500 | 0·063 | 0·033 | 0·131 |
| ,, | Centre of head | 0·480 | 0·014 | 0·494 | 0·089 | 0·041 | 0·152 |
| ,, | Neck .. .. | 0·456 | 0·009 | 0·500 | 0·079 | 0·037 | 0·130 |
| ,, | Base .. .. | 0·472 | 0·014 | 0·511 | 0·076 | 0·035 | 0·110 |
| 363 | Surface.. .. | 0·357 | 0·010 | 0·412 | 0·057 | 0·039 | 0·122 |
| ,, | Centre of head | 0·501 | 0·006 | 0·430 | 0·099 | 0·057 | 0·139 |
| ,, | Neck .. .. | 0·507 | 0·011 | 0·430 | 0·102 | 0·063 | 0·126 |
| ,, | Base .. .. | 0·459 | 0·014 | 0·407 | 0·063 | 0·033 | 0·105 |
| 4275 | Surface.. .. | 0·297 | 0·012 | 0·442 | 0·028 | 0·018 | 0·134 |
| ,, | Centre of head | 0·504 | 0·016 | 0·500 | 0·062 | 0·048 | 0·152 |
| 4164 | Surface.. .. | 0·387 | 0·008 | 0·494 | 0·027 | 0·017 | 0·134 |
| ,, | Centre of head | 0·441 | 0·007 | 0·506 | 0·046 | 0·027 | 0·137 |
| 5469 | Surface.. .. | 0·351 | 0·028 | 1·146 | 0·045 | 0·019 | 0·140 |
| ,, | Centre of head | 0·681 | 0·023 | 1·239 | 0·084 | 0·021 | 0·135 |

Portions immediately adjacent may, however, also exhibit a very variable composition. This is well known in the case of the carbon percentage of cement steel and of manufactured steel (being in the former greater at the surface, and in the latter less than in the interior), in the case of graphite (especially in mottled pig iron), and in

[*] Read before the Iron and Steel Institute.

that of slag (notably in weld iron). Other elements, such as manganese, phosphorus, and especially sulphur, may also, however, in certain circumstances, be very unequally distributed (*Oesterr. Zeitschr. für Berg- und Hüttenwesen*, 1896, p. 159). In the case of phosphorus determinations by eight different chemists, in one and the same pig iron, the highest result was about double as great as the lowest. In a pig iron sixteen chemists found, as is shown by the following figures (*Journ. Anal. and Applied Chem.*), from 0·005 to 0·024 per cent of sulphur, and the very highest and lowest of these results were obtained by chemists of high repute :—

| | Sulphur, per cent. |
|---|---|
| *a.* Aqua regia method .. .. .. .. .. | 0·005 |
| *b.* Absorption and oxidation with bromine, treatment of the insoluble residue with aqua regia, barium sulphate precipitate weighed .. .. .. .. .. .. .. | 0·008 |
| *c.* Absorption and titration with normal iodine solution.. .. .. .. .. .. .. | 0·009 |
| *d.* Method not specified .. .. .. .. .. | 0·010 |
| *e.* Absorption in alkaline solution of lead nitrate and weighing the precipitate as barium sulphate .. .. .. .. .. .. | 0·011 |
| *f.* Aqua regia method ; the solution was allowed to stand twenty-four hours after the addition of barium chloride.. .. .. | 0·012 |
| *g.* Aqua regia method .. .. .. .. .. | 0·012 |
| *h.* Absorption in potassium permanganate solution, and weighing the barium sulphate precipitate.. .. .. .. .. .. | 0·013 |
| Absorption in cadmium solution and titration with normal iodine solution .. .. | 0·013 |
| *j.* Potassium permanganate solution and barium sulphate weighed .. .. .. .. | 0·013 |
| *k.* Aqua regia method. Neutralised with ammonia. Precipitation of barium sulphate and allowed to stand for twenty-four hrs. | 0·013 |
| *l.* Absorption in cadmium chloride solution and titration with normal iodine solution | 0·015 |
| *m.* Absorption and titration with normal iodine solution.. .. .. .. .. .. .. .. | 0·017 |
| *n.* Absorption in potassium permanganate solution and weighing the barium sulphate | 0·017 |
| *o.* Volumetric analysis (details not specified). | 0·019 |
| *p.* Absorption in cadmium sulphate and titration with normal iodine solution .. .. | 0·020 |
| *q.* Aqua regia method .. .. .. .. .. | 0·021 |
| *r.* Absorption in caustic soda solution and titration with normal iodine solution .. | 0·022 |
| *s.* Aqua regia method .. .. .. .. .. | 0·024 |

(To be continued).

## ON THE
## AMOUNT OF GOLD AND SILVER IN SEA-WATER.[*]

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Continued from p. 148).

### Southern Sea-waters.

IN examining the southern sea-waters, in the first batch a litre of each was treated, and the characteristic reaction for gold obtained from Nos. 1, 2, 4, 5, 6. In the next batch of two litres each, 1, 2, 3, and 5 showed the presence of gold ; the films were treated a second time with chlorine water, when Nos. 3, 4, and 5 gave the gold reaction. In the third batch, Nos. 1, 2, 3, and 6 reacted for gold, and on a second treatment Nos. 3 and 6 again gave the reaction for gold. The details are as follows :—

[*] Read before the Royal Society of N. S. Wales.

No. 1, South—Collected November 26, 1894, one mile east of South Head Lighthouse. Latitude 33° 43′ S.

Test No. 1.—Upon 1 litre. SnCl$_2$ was added on Dec: 11, 1894, a white sediment was formed ; this, on Feb. 8, 1895, had changed to a slate colour ; the slate colour was probably due to the presence of gold.

Test No. 2.—Upon 2 litres. December 22, 1894, the white precipitate on February 8, 1895, showed a pinkish ring at upper part, evidently due to the presence of gold. The film from the ferrous sulphate was extracted a second time with Cl water, on December 31 ; the solution became opalescent on the addition of the HCl and SnCl$_2$, and acquired a bluish tinge (probably due to gold), but by February 8 this blue tint had disappeared and only a white sediment remained.

Test No. 3.—Upon 1500 c.c. June 12, 1895. On June 21 the white precipitate showed a pinkish layer at the top $\frac{1}{8}$ inch deep, the pink colour was more decided on the 24th. On July 3 and 4 it began to turn violet, and on July 7 was of a distinct violet tint, and on July 10 the upper part of the precipitate had darkened to a purple colour, which was doubtless due to the presence of gold.

No. 2, South—Collected November 26, 1894, three miles off Bulli. Latitude about 34°.

Test No. 1.—Gave a slight white sediment ; on Feb. 8 this was yellowish with a dark reddish brown ring.

Test No. 2.—On 2 litres. Put up on December 22, 1894. On December 31 the sediment was white ; but had acquired a pinkish tinge on the surface by February 8, 1895. The iron oxide film was extracted a second time with Cl water on December 31 ; this gave a brownish coloured solution and a white precipitate, which had not changed by February 8.

Test No. 3.—Upon 1500 c.c. June 12, 1895. On July 6 there was a slight red tint on the sediment, and on July 10 this had become brown.

No 3, South—Collected November 27, 1894, five miles from Black Head, Shoalhaven Bight. Latitude about 34°.

Test No. 1.—Upon 1 litre. Clear bluish tinge, sediment slightly coloured.

Test No. 2.—On 2 litres. A slight amethyst tint within three minutes after adding the SnCl$_2$. On February 8, 1895, the sediment was bluish below with the pink colour above unchanged. The second Cl water extract of the film, on adding the SnCl$_2$, became opalescent with a faint amethyst tinge ; on February 8, 1895, the sediment was white with light reddish brown ring.

Test No. 3.—1900 c.c. June 21, 1895. A buff sediment with a pinkish tint at top ; on the 24th the pink tint was deeper, a pale violet on July 3, and on July 6 had become a full violet ; on July 10 this had become purple—the buff below remaining unchanged.

No. 4, South—Collected November 27, 1894, from one mile off Cape St. George Lighthouse, Jervis Bay. Latitude about 35° S.

Test No. 1.—Upon 1 litre. December 11, 1894. After standing 5 hours the solution was clear with a bluish tinge ; sediment slightly coloured. On February 8, 1895, the white sediment was marked by a reddish ring.

Test No. 2.—Two litres, on December 22, 1894. No colour on the 29th nor on February 8, 1895. Nor from the second Cl water extract ; afterwards yielded a bluish tinge with pinkish colour to sediment.

Test No. 3.—1900 c.c. June 21, 1895. A bluish tinge on top of white sediment observed July 5, 1895.

No. 5, South—Collected November 27, 1894, from two miles off Brush Island. Latitude about 35° 5′ S.

Test No. 1.—Upon 1 litre. December 11, 1894. Clear bluish tinge ; on February 8, 1895, the white sediment showed a bright pink ring.

Test No. 2.—Gave no indication of gold, neither did the second Cl water extract.

Test No. 3.—1300 c.c. June 21, 1895. On addition of the stannous chloride this gave a bluish tinge; on July 10 the white sediment was almost black at the base.

No. 6, South—Collected November 28, 1894. From twenty-seven miles off Broulee, near Moruya. Latitude about 36° 5′ S.

Test No. 1.—Upon 1 litre. December 11, 1894. No colour until February 8, 1895, when the light brown sediment showed a reddish ring.

Test No. 2.—Upon 2 litres. Amethyst tinge. Second extract with Cl water gave a bluish tinge and the sediment had a slight pink colouration.

Test No. 3.—1225 c.c. June 21, 1895. On June 24 the white sediment showed a pink tinge at top one-sixteenth inch deep; on July 10, 1895, the sediment was pale brown with an onyx-like layer near the top, with faint purple tinge.

On April 3, 1895, the precipitate in each test-tube of the first batch of southern waters had changed to a dirty, almost black, colour, i.e., after an interval of nearly four months from the initiation of the experiment, viz., from December 18, 1894, to April 3, 1895.

It was noticed, in some instances, that after long standing the pink or violet tint gradually faded, especially on the side exposed to the brighter light of the window; in some cases the colour disappeared totally.

*Northern Sea-waters.*

No. 1.—Collected February 19th, 1895, about 1½ miles off Sandy Point, Richmond River, Lat. about 28° S.

No. 2.—Collected at North Solitary, Lat. about 29° S., February 19th, a strong southerly current.

No. 3.—From about 4 miles off Smoky Cape, Lat. about 30°, on February 20th.

No. 4.—From 2 miles off Tacking Point, Lat. about 31° 30′, February 20th.

No. 5.—From 2 miles off Cape Hawke, Lat. about 32° 2′, February 20th.

No. 6.—About 5 miles off Port Stephens, Lat. about 33°, February 20th.

All six samples of northern sea-waters also gave the reaction for gold; the details are omitted for brevity. As in the case of the southern samples, some gave the reaction readily, others required from one to several weeks. I should not, however, like to say that this is a sufficient indication of some being richer than others, for the test appears to be wanting in precision.

(To be continued).

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 9, August 31, 1896.

Doubling Back of the X Rays behind Opaque Bodies.—Emile Villari.—When studying the transparency of metals to the X rays I interposed leaves of them between a pear-shaped Crookes tube and a charged electroscope. In numerous experiments I observed that the electroscope was always discharged, even if it was placed in the full shadow of the rays produced by ample metallic screens, perfectly opaque. This fact made me suppose that the rays, or their efficiency, were doubled back in the shadow of opaque bodies so as to strike the electroscope and discharge it. From further experiments it resulted that, to discharge the electroscope it is not necessary that it should be struck directly by the X rays, since it is sufficient if the air which has been traversed by them arrives there. In fact, the electroscope is rapidly discharged from 10° in twenty-eight seconds, if the air which has been traversed by the rays is driven against it by means of a blast. On the contrary, when the Crookes tube is inactive the air driven against the electroscope exerts no action. Therefore we may say that the X rays give to air the activity necessary to discharge the electroscope—an activity which is preserved for a certain time.

Researches on Double Chlorides.—Raoul Varet.—The compounds formed by mercuric chloride when uniting with other metallic chlorides have, in the dissolved state, formation heats which are of the same order of magnitude for one and the same series of double salts. The formation of compounds produced by the chlorides of kindred metals give rise therein to effects which are sensibly equal. Dialysis shows that these combinations are partly dissociated in the midst of their solutions. These data lead us to regard these double salts as being derivatives of sparingly stable complex acids, such as $Hg_2Cl_6H_2$ and $HgCl_4H_2$. The double salts formed by the chlorides of copper, cadmium, &c., are dissociated by dialysis. Their formation in the dissolved state only gives rise to very feeble thermic effects.

Action of the Soluble Oxidising Ferment of Mushrooms upon Phenols Insoluble in Water.—Emile Bourquelot.—Three xylenols have been tried, dissolved in 0·50 grm. of absolute alcohol and 50 c.c. of water. With orthoxylenol there was produced a white precipitate turning to a salmon colour. With metaxylenol the precipitate was also white, becoming a dirty rose. The precipitate dissolves in ether with a deep yellow colour. With paraxylenol there is produced a rosy white precipitate, insoluble in ether. Naphthols α and β are also oxidised. Naphthol α colours the liquid violet, passing then to blue, and then forming a dirty blue precipitate. The precipitate is partially stable in ether, with a mauve colour. With naphthol β there is formed a white precipitate, which gradually turns yellow. This precipitate is almost entirely soluble in ether, which takes a deep yellow colour.

Congelation-point of Cows' Milk.—MM. Bordas and Génin.—Some chemists have asserted that the congelation-point of milk is constant, so that the addition of water can thus be detected. The authors, on the contrary, find that the congelation-point of milk is variable and cannot be used to detect sophistication with water.

# MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) at the Liverpool Meeting of the British Association :—

*President*—Dr. Ludwig Mond, F.R.S.

*Vice-Presidents*—Sir F. Abel, F.R.S.; Prof. J. Campbell Brown; Prof. J. Dewar, F.R.S.; Dr. J. H. Gladstone, F.R.S.; Dr. A. G. Vernon Harcourt, F.R.S.; Prof. R. Meldola, F.R.S.; E. K. Muspratt; Prof. W. Ramsay, F.R.S.; Sir H. E. Roscoe, F.R.S.; Dr. T. E. Thorpe, F.R.S.

*Secretaries*—Arthur Harden (Recorder); Charles A. Kohn.

*Committee*—A. H. Allen; G. H. Bailey; Prof. M. Bamberger; Prof. P. P. Bedson; C. H. Bothamley; Eustace Carey; A. Chance; Prof. F. Clowes; C. F. Cross; Prof. A. E. Dixon; Prof. H. B. Dixon, F.R.S.; Prof. J. J. Dobbie; W. R. Dunstan, F.R.S.; T. Fairley; A. E. Fletcher; F. H. Gossage; F. Hurter; B. Lean; Prof. Oscar Liebreich; Prof. Liversidge, F.R.S.; Stevenson Macadam; Prof. H. McLeod, F.R.S.; H. Marshall; R. Mond; H. Forster Morley; D. H. Nagel; Manning Prentice; H. Ramage; J. B. Readman; A. Rée; A. Scott; E. Schunck, F.R.S.; S. Shaw; Prof. H. Lloyd Snape; A. Smith; Prof. A. Smithells; Prof. J. Smythe; W. Thomson; M. Wildermann; Prof. W. C. Williams; V. H. Veley, F.R.S.; J. W. Thomas; G. Young.

The Papers brought before the Section were as follows:—

President's Address.

*Prof. H. B. Dixon*—Reflected Waves in the Explosion of Gases.

*Dr. J. H. Gladstone* and *W. Hibbert*—Action of Metals and their Salts on the Ordinary and Röntgen Rays: a Contrast.

*Prof. F. Clowes*—Limiting Explosive Proportions of Acetylene, and Detection and Measurement of the Gas in the Air.

*Prof. F. Clowes*—The Accurate Determination of Oxygen by Absorption with Alkaline Pyrogallol Solution.

*Dr. A. W. Titherley*—The Amides of the Alkali Metals and some of their Derivatives.

*D. H. Nagel*—Report of the Committee on the Bibliography of Spectroscopy.

*Prof. J. Hummel*—Report of the Committee on the Action of Light on Dyed Colours.

*C. F. Cross*—Report of the Committee on the Carbohydrates of Barley Straw.

*Prof. Oscar Liebreich*—Diminution of Chemical Action resulting from Limitations of Space.

*Prof. M. Bamberger*—Excrescent Resins.

*Prof. P. P. Bedson*—Report of the Committee to Inquire into the Proximate Chemical Constituents of the various kinds of Coal.

*Dr. M. Wildermann*—The Velocity of Reactions before perfect Equilibrium takes place.

*Dr. T. Bradshaw*—The Behaviour of Litmus in Amphoteric Solutions.

*A. G. Green* and *A. Wahl*—Constitution of Sun Yellow or Curcumine and Allied Colouring Matters.

*Dr. F. E. Francis*—Abnormalities in the Behaviour of Ortho-derivatives of *o*-Amido and Nitro-benzylamine.

*Dr. W. Newton*—Nitrates: their Occurrence and Manufacture.

*Prof. Ramsay*—Helium.

*Prof. M. Bamberger*—The presence of Argon in the Gases of an Austrian Well.

*Dr. F. Hurter*—The Manufacture of Chlorine by means of Nitric Acid.

*Prof. J. Dewar*—Low Temperature Research.

Report of the Committee on Electrolytic Analysis.

*Dr. C. A. Kohn*—A Modified Form of Schrötter's Apparatus.

*Dr. C. A. Kohn* and *Dr. T. L. Bailey*—A New Form of Aspirator.

*Dr. J. Haldane*—The Detection and Estimation of Carbon Monoxide in Air.

*Prof. F. Clowes*—Detection of Minute Quantities of Carbon Monoxide by the Flame-cap Test.

*Sir H. E. Roscoe*—Chemical Education in England and Germany.

*Dr. J. H. Gladstone*—Report of the Committee on the Teaching of Science in Elementary Schools.

*L. Edna Walter*—The Teaching of Science in Girls' Schools.

**Separation of Bismuth from the Metals of the Copper and the Iron Group by Heating their Salts in a Current of Dry Hydrochloric Acid.**—P. Jannasch and S. Grosse (a Preliminary Communication).—In carrying out a great number of separations of arsenic from the metals of the copper and the iron group, of which we shall give account on opportunity, we made the observation that bismuth also, under suitable experimental conditions, can be easily and completely volatilised from mixtures of metallic salts, in a current of dry hydrochloric acid, at a relatively low temperature, thus showing a behaviour quite analogous to that of tin. This fact, as we have established, renders it possible to separate bismuth quantitatively from a series of less readily volatile metallic chlorides. We have already taken in hand analyses of this kind.—*Zeitsch. f. Anorganische Chemie*, vol. xii., Part 5, p. 398.

# THE CHEMICAL NEWS.

## Vol. LXXIV., No. 1923.

ADDRESS TO THE CHEMICAL SECTION
OF THE
BRITISH ASSOCIATION.

LIVERPOOL, 1896.

By Dr. LUDWIG MOND, F.R.S., President of the Section.

(Concluded from p. 158).

MR. DEACON came to the conclusion that if a mixture of hydrochloric acid with atmospheric air was heated in the presence of a suitable substance capable of initiating the interaction of these two gases by its affinity to both, it would to a very great extent be converted into chlorine with the simultaneous formation of steam, because the formation of steam from oxygen and hydrogen gives rise to the evolution of a considerably larger quantity of heat than the combination of hydrogen and chlorine. Mr. Deacon found that the salts of copper were a very suitable substance for this purpose, and took out a patent for this process in 1868. He entrusted the study of the theoretical and practical problems connected with this process to Dr. Ferdinand Hurter, who carried them out in a manner which will always remain memorable and will never be surpassed, as an example of the application of scientific methods to manufacturing problems, and which soon placed this beautiful and simple process on a sound basis as a manufacturing operation.

In the ordinary course of manufacture the major part—about two-thirds—of the hydrochloric acid is obtained mixed with air and a certain amount of steam, but otherwise very little contaminated. Instead of condensing the muriatic acid from this mixture of gases by bringing it into contact with water, Mr. Deacon passed it through a long series of cooling pipes to condense the steam, which of course absorbed hydrochloric acid, and formed a certain quantity of strong muriatic acid. The mixture of gases was then passed through an iron superheater to raise it to the required temperature, and thence through a mass of broken bricks impregnated with sulphate or chloride of copper contained in a chamber or cylinder called a decomposer, which was protected from loss of heat by being placed in a brick furnace kept sufficiently hot. In this apparatus from 50 to 60 per cent of the hydrochloric acid in the mixture of gases was burnt to steam and chlorine. In order to separate this chlorine from the steam and the remaining hydrochloric acid the gases were washed with water, and subsequently with sulphuric acid. The mixture now consisted of nitrogen and oxygen, containing about 10 per cent of chlorine gas, which could be utilised without any difficulty in the manufacture of bleach liquors and chlorate of potash, and which Mr. Deacon also succeeded in using for the manufacture of bleaching powder, by bringing it into contact in specially constructed chambers with large surfaces of hydrate of lime. Within recent years this latter object has been attained in a more expeditious and perfect manner by continuous mechanical apparatus (of which those constructed by Mr. Robert Hasenclever and Dr. Carl Langer have been the most successful), in which the hydrate of lime is transported in a continuous stream by single or double conveyors in an opposite direction to the current of dilute chlorine, and the bleaching powder formed delivered direct into casks, thereby avoiding the intensely disagreeable work of packing this offensive substance by hand.

Mr. Deacon's beautiful and scientific process thus involves still less movement of materials than the very simple process of Mr. Weldon, because, in lieu of large volumes of liquids, he only moves a current of gas through his apparatus, which requires a minimum of energy. The only raw material used for converting hydrochloric acid into chlorine is atmospheric air, the cheapest of all at our command. The hydrochloric acid which has not been converted into chlorine by the process is all obtained, dissolved in water, as muriatic acid, and is not lost, as in previous processes, but is still available to be converted into chlorine by other methods, or to be used for other purposes.

In spite of these distinct advantages, this process took a long time before it became adopted as widely as it undoubtedly deserved. This was mainly due to the fact that the economy in the use of muriatic acid which it effected was at the time when the process was brought out, and for many years afterwards, no object to the majority of chlorine manufacturers, who were still producing more of this commodity than they could use. Moreover, there were other reasons. The plant required for this process, although so simple in principle, is very bulky in proportion to the quantity of chlorine produced, and, as I have pointed out, the process only succeeded in converting about one-third of the hydrochloric acid produced into chlorine, the remainder being obtained as muriatic acid, which had in most instances to be converted into chlorine by the Weldon process; so that the Deacon process did not constitute an entirely self-contained method for this manufacture. This defect, of small moment as long as muriatic acid was produced in excessive quantities, was only remedied by an invention of Mr. Robert Hasenclever a short number of years ago; when by the rapid development of the ammonia soda process the previously existing state of things had been completely changed, and when, at least on the Continent, muriatic acid was no longer an abundant and valueless by-product, but, on the contrary, the alkali produced by the Le Blanc process had become a by-product of the manufacture of chlorine. Mr. Hasenclever, in order to make the whole of the muriatic acid he produces available for conversion into chlorine by the Deacon process, introduces the liquid muriatic acid in a continuous stream into hot sulphuric acid contained in a series of stone vessels, through which he passes a current of air. He thus obtains a mixture of hydrochloric acid and air, well adapted for the Deacon process, the water of the muriatic acid remaining with the sulphuric acid, from which it is subsequently eliminated by evaporation. In this way the chlorine in the hydrochloric acid can be almost entirely obtained in its free state by the simplest imaginable means, and with the intervention of no other chemical agent than atmospheric air. Since their introduction the Deacon process has supplanted the Weldon process in nearly all the largest chlorine works in France and Germany, and is now also making very rapid progress in this country.

Mr. Weldon, when he decided to give up his manganite of magnesia process, by no means relaxed his efforts to work out a chlorine process which should utilise the whole of the muriatic acid. While working with manganite of magnesia he found that magnesia alone would answer the purpose without the presence of the peroxide of manganese. He obtained the assistance of M. Pechiney, of Salindres, and in conjunction with him worked out what has become known as the "Weldon-Pechiney" process, which was first patented in 1884.

This process consists in neutralising muriatic acid by magnesia, concentrating the solution to a point at which it does not yet give off any hydrochloric acid, and then mixing into it a fresh quantity of magnesia so as to obtain a solid oxychloride of magnesium. This is broken up into small pieces, which are heated up rapidly to a high temperature without contact with the heating medium, while a current of air is passing through them. The oxychloride of magnesium containing a large quantity of water, this treatment yields a mixture of chlorine and hydrochloric acid with air and steam, the same as the Deacon process, and this is treated in a very similar way

to eliminate the steam and the acid from the chlorine. The acid condensed is, of course, treated with a fresh quantity of magnesia, so that the whole of the chlorine which it contains is gradually obtained in the free state.

The rapid heating to a high temperature of the oxy-chloride of magnesium without contact with the heating medium was an extremely difficult practical problem, which has been solved by M. Pechiney and his able assistant, M. Boulouvard, in a very ingenious and entirely novel way.

They lined a large wrought-iron box with fire-bricks, and built inside of this vertical fire-brick walls with small empty spaces between them, thus forming a number of very narrow chambers, so arranged that they could all be filled from the top of the box and emptied from the bottom. These chambers they heated to a very high temperature by passing a gas flame through them, thus storing up in the brick walls enough heat to carry out and complete the decomposition of the magnesium oxy-chloride, with which the chamber was filled when hot enough.

Mr. Weldon himself called this apparatus a "baker's oven," in which trade certainly the same principle has been employed from time immemorial; but to my know-ledge it had never before been used in any chemical industry. This process has been at work at M. Pechiney's large alkali works at Salindres, and is now at work in this country at the chlorate of potash works of Messrs. Allbright and Wilson at Oldbury, a manufacture for which it offers special advantages. Mr. Weldon and M. Pechi-ney had expected that this process would become spe-cially useful in connection with the ammonia soda process by preparing, in the way proposed by Mr. Solvay and Mr. Weldon in 1872, a solution of magnesium chloride as a by-product of this manufacture; but instead of obtaining muriatic acid from this solution by Clemm's process, to treat it by the new process, so as to obtain the bulk of the chlorine at once in the free state. But M. Pechiney did no more succeed than his predecessors in recovering the ammonia by means of magnesia in a satisfactory way.

Quite recently, however, it has been applied to obtain chlorine in connection with the ammonia soda process by Dr. Pick, of Czakowa, in Austria. He recovers the ammo-nia, as usual, by means of lime, and converts the solution of chloride of calcium, obtained by a process patented by Mr. Weldon in 1869, viz., by treatment with magnesia and carbonic acid under pressure, into chloride of mag-nesium with the formation of carbonate of lime. The magnesium chloride solution is then concentrated and treated by the Weldon-Pechiney process.

I have repeatedly referred during this brief history to the great change which has been brought about in the position of chlorine manufacture by the development of the ammonia soda process, and have pointed out that the muriatic acid which for a long time was the by-product of the Le Blanc process, without value, thereby became gra-dually its main and most valuable product, while the alkali became its by-product.

I have told you how, very early in the history of this process, Mr. Solvay and Mr. Weldon proposed means to provide for this contingency, and how Mr. Weldon con-tinued to improve these means until the time of his death. Mr. Solvay, on his part, also followed up the subject with that tenacity and sincerity of purpose which distinguishes him, his endeavours being mainly directed to producing chlorine direct from the chloride of calcium running away from his works by mixing it with clay and passing air through the mixture at very high temperatures, thus pro-ducing chlorine and a silicate of calcium, which could be utilised in cement-making. The very high tempera-tures required prevented, however, this process from becoming a practical success.

I have already told you what a complicated series of operations Dr. Pick has lately resorted to in order to obtain the chlorine from this chloride of calcium. Yet the problem of obtaining chlorine as a by-product of the ammonia soda process presents itself as a very simple one.

This process produces a precipitate of bicarbonate of soda and a solution of chloride of ammonium by treating natural brine or an artificially made solution of salt, in which a certain amount of ammonia has been dissolved, with carbonic acid. In their original patent of 1838 Messrs. Dyar and Herring proposed to evaporate this solution of ammonium chloride, and to distil the resulting dry product with lime to recover the ammonia. Now all that seemed to be necessary to obtain the chlorine from this ammonium chloride was to substitute another oxide for lime in the distillation process, which would liberate the ammonia and form a chloride which on treatment with atmospheric air would give off its chlorine and re-produce the original oxide. The whole of the reactions for producing carbonate of soda and bleaching powder from salt would thus be reduced to their simplest possible form; the solution of salt, as we obtain it in the form of brine direct from the soil, would be treated with ammonia and carbonic acid to produce bicarbonate and subsequently monocarbonate of soda, the limestone used for producing the carbonic acid would yield the lime required for ab-sorbing the chlorine, and produce bleaching powder instead of being run into the rivers in combination with chlorine in the useless form of chloride of calcium, and both the ammonia used as an intermediary in the produc-tion of soda and the metallic oxide used as an inter-mediary in the production of chlorine would be continuously recovered.

The realisation of this fascinating problem has occu-pied me for a great many years. In the laboratory I obtained soon almost theoretical results. A very large number of oxides and even of salts of weak acids were found to decompose ammonium chloride in the desired way; but the best results (as was to be clearly antici-pated from thermo-chemical data) were given by oxide of nickel.

When, however, I came to carry this process out on a large scale, I met with the most formidable difficulties, which it took many years to overcome successfully.

The very fact that ammonium chloride vapour forms so readily metallic chlorides when brought in contact at an elevated temperature with metals or oxides, or even sili-cates, led to the greatest difficulty, viz., that of con-structing apparatus which would not be readily destroyed by it.

Amongst the metals we found that platinum and gold were the only ones not attacked at all. Antimony was but little attacked, and nickel resisted very well if not exposed to too high a temperature, so that it could be, and is being, used for such parts of the plant as are not directly exposed to heat. The other parts of the apparatus coming in contact with the ammonium chloride vapour I ultimately succeeded in constructing of cast and wrought iron, lined with fire-bricks or Doulton tiles, the joints between these being made by means of a cement consisting of sulphate of baryta and water-glass.

After means had been devised for preventing the breaking of the joints through the unequal expansion of the iron and the earthenware, the plant so constructed has lasted very well.

Oxide of nickel, which had proved the most suitable material for the process in the laboratory, gave equally good chemical results on the large scale, but occasionally a small quantity of nickel chloride was volatilised through local over-heating, which, however, was sufficient to gra-dually make up the chlorine conduits. We therefore looked out for an active material free from this objection. Theoretical considerations indicated magnesia as the next best substance, but it was found that the magnesium chloride formed was not anhydrous, but retained a certain amount of the steam formed by the reaction, which gave rise to the formation of a considerable quantity of hydro-chloric acid on treatment with hot air. In conjunction with Dr. Eschellman (who carried out the experiments

for me), I succeeded in reducing the quantity of this hydrochloric acid to a negligible amount by adding to the magnesia a certain amount of chloride of potassium, which probably has the effect of forming an anhydrous double chloride.

This mixture of magnesia and potassium chloride is, after the addition of a certain quantity of china clay, made into small pills, in order to give a free and regular passage throughout their entire mass to the hot air and other gases with which they have to be treated. In order to avoid as far as possible the handling and consequent breaking of these pills, I vapourise the ammonium chloride in a special apparatus, and take the vapours through these pills and subsequently pass hot air through, and then again ammonium chloride vapour, and so on, without the pills changing their place.

The vapourisation of the ammonium chloride is carried out in long cast-iron retorts lined with thin Doulton tiles, and placed almost vertically in a furnace which is kept by producer gas at a very steady and regular temperature. These retorts are kept nearly full with ammonium chloride, so as to have as much active heating surface as possible. From time to time a charge of ammonium chloride is introduced through a hopper at the top of these retorts, which is closed by a nickel plug. The ammonium chloride is very pure, being crystallised out from its solution as produced in the ammonia soda manufacture by a process patented by Mr. Gustav Jarmay, which consists in lowering the temperature of these solutions considerably below 0° C. by means of refrigerating machinery. The retorts will therefore evaporate a very large amount of ammonium chloride before it becomes necessary to take out through a door at their bottom the non-volatile impurities which accumulate in them. The ammonium chloride vapour is taken from these retorts by cast-iron pipes lined with tiles and placed in a brick channel, in which they are kept hot, to prevent the solidification of the vapour, to large upright wrought-iron cylinders which are lined with a considerable thickness of fire-bricks, and are filled with the magnesia pills, which are, from the previous operations, left at a temperature of about 300° C. On its passage through the pills the chlorine in the vapours is completely retained by them, the ammonia and water vapour formed pass on and are taken to a suitable condensing apparatus. The reaction of the ammonium chloride vapour upon magnesia being exo-thermic, the temperature of the pills rises during this operation, and no addition of heat is necessary to complete it. The temperature, however, does not rise sufficiently to satisfactorily complete the second operation, viz., the liberation of the chlorine and the re-conversion of the magnesium chloride into magnesium oxide by means of air. This reaction is slightly endo-thermic, and thus absorbs a small amount of heat, which has to be provided in one way or another. I effect this by heating the pills to a somewhat higher temperature than is required for the action of the air upon them, viz., to 600° C., by passing through them a current of a dry inert gas free from oxygen, heated by a Siemens-Cowper stove to the required temperature. I use for this purpose the gas leaving the carbonating plant of the ammonia soda process.

This current of gas also carries out of the apparatus the small amount of ammonia which was left in between the pills. It is washed to absorb this ammonia, and, after washing, this same gas is passed again through the Siemens-Cowper stove, and thus constantly circulated through the apparatus, taking up the heat from the stove and transferring it to the pills. When these have attained the required temperature, the hot inert gas is stopped and a current of hot air passed through, which has also been heated to 600° C. in a similar stove. The air acts rapidly upon the magnesium chloride, and leaves the apparatus charged with 18 to 20 per cent of chlorine and a small amount of hydrochloric acid. The chlorine comes gradually down, and when it has reached about 3 per cent

the temperature of the air entering the apparatus is lowered to 350° C. by the admixture of cold air to the hot air from the stove; and the weak chlorine leaving the apparatus is passed through a second stove, in which its temperature is raised again to 600° C., and passed into another cylinder full of pills which are just ready to receive the hot-air current. A series of four cylinders is required to procure the necessary continuity for the process.

The chlorine gas is washed with a strong solution of chloride of calcium, which completely retains all the hydrochloric acid, and is then absorbed in an apparatus invented by Dr. Carl Langer, by hydrate of lime, which is made to pass by a series of interlocked transporting twin-screws in an opposite direction to the current of gas, and produces very good and strong bleaching powder, in spite of the varying strength of the chlorine gas. The hydrochloric acid absorbed by the solution of calcium chloride can, by heating this solution, be readily driven out and collected.

This process has now been in operation on a considerable scale at our works at Winnington for several years, with constantly improving results, notably with regard to the loss of ammonia, which has gradually been reduced to a small amount. The process has fully attained my object, viz., to enable the ammonia soda process to compete not only in the production of carbonate of soda, but also in the production of bleaching powder, with the Le Blanc process.

Nevertheless, I have hesitated to extend this process as rapidly as I should otherwise have done, because, very shortly after I had overcome all its difficulties, entirely different methods from those hitherto employed for the manufacture of chlorine were actively pushed forward in different parts of the globe, for which great advantages were claimed, but the real importance and capabilities of which were—and are up to this date—very difficult to judge. I refer to the processes for producing chlorine by electrolysis.

During the first decade of this century Humphry Davy had, by innumerable experiments, established all the leading facts concerning the decomposing action of an electric current upon chemical compounds. Amongst these he was the first to discover that solutions of alkaline chlorides, when submitted to the action of a current, yield chlorine. His successor at the Royal Institution, Michael Faraday, worked out and proved the fundamental law of electrolysis, known to everybody as "Faraday's Law," which has enabled us to calculate exactly the amount of current required to produce by electrolysis any definite quantity of chlorine. Naturally, since these two eminent men had so clearly shown the way, numerous inventors have endeavoured to work out processes based on these principles for the production of chlorine on a manufacturing scale, but only during the last few years have these met with any measure of success.

It has taken all this time for the classical work of Faraday on electro-magnetism to develop into the modern magneto-electric machine, capable of producing electricity in sufficient quantity to make it available for chemical operations on a large scale; for you must keep in mind that an electric installation sufficient to light a large town will only produce a very moderate quantity of chemicals.

In applying electricity to the production of chlorine, various ways have been followed, both as to the raw materials and as to the apparatus employed. While most inventors have proposed to electrolyse a solution of chloride of sodium, and to produce thereby chlorine and caustic soda, I am not aware that up to this day any quantity of caustic soda made by electrolysis has been put on to the market.

Only two electrolytic works producing chlorine on a really large scale are in operation to-day. Both electrolyse chloride of potassium, producing as a by-product caustic potash, which is of very much higher value than

caustic soda, and of which a larger quantity is obtained for the same amount of current expended. These works are situated in the neighbourhood of Stassfurt, the important centre of the chloride of potassium manufacture. The details of the plant they employ are kept secret, but it is known that they use cells with porous diaphragms of special construction, for which great durability is claimed. There are at this moment a considerable number of smaller works in existence, or in course of erection in various countries, intended to carry into practice the production of chlorine by electrolysis by numerous methods, differing mainly in the details of the cells to be used, but some of them also involving what may be called new principles. The most interesting of these are the processes in which mercury is used alternately as cathode and anode, and salt as electrolyte. They aim at obtaining in the first instance chlorine and an amalgam of sodium, and subsequently converting the latter into caustic soda by contact with water, which certainly has the advantage of producing a very pure solution of caustic soda. Mr. Hamilton Castner has carried out this idea most successfully by a very beautiful decomposing cell, which is divided into various compartments, and so arranged that by slightly rocking the cell the mercury charged with sodium in one compartment passes into another, where it gives up the sodium to water, and then returns to the first compartment to be re-charged with sodium. His process has been at work on a small scale for some time at Oldbury, near Birmingham, and works for carrying it out on a large scale are now being erected on the banks of the Mersey, and also in Germany and America.

Entirely different from the foregoing, but still belonging to our subject, are methods which propose to electrolyse the chlorides of heavy metals (zinc, lead, copper, &c.) obtained in metallurgical operations or specially prepared for the purpose, among which the processes of Dr. Carl Hoepfner deserve special attention. They eliminate from the electrolyte immediately both the products of electrolysis, chlorine on one side and zinc and copper on the other, and thus avoid all secondary reactions, which have been the great difficulty in the electrolysis of alkaline chlorides.

All these processes have, however, still to stand the test of time before a final opinion can be arrived at as to the effect they will have upon the manufacture of chlorine, the history of which we have been following, and this must be my excuse for not going into further details. I have endeavoured to give you a brief history of the past of the manufacture of chlorine, but I will to-day not attempt to deal with its future! Yet I cannot leave my subject without stating the remarkable fact that every one of these processes which I have described to you is still at work to this day, even those of Scheele and Berthollet, all finding a sphere of usefulness under the widely varying conditions under which the manufacture of chlorine is carried on in different parts of the world.

Let me express a hope that a hundred years hence the same will be said of the processes now emerging and the processes still to spring out of the inventor's mind. Rapid and varied as has been the development of this manufacture, I cannot suppose that its progress is near its end, and that Nature has revealed to us all her secrets as to how to procure chlorine with the least expenditure of trouble and energy. I do not believe that industrial chemistry will in future be diverted from this Section and have to wander to Section A under the ægis of applied electricity. I do not believe that the easiest way of effecting chemical changes will ultimately be found in transforming heat and chemical affinity into electricity, tearing up chemical compounds by this powerful medium, and then to re-combine their constituents in such form as we may require them. I am sure there is plenty of scope for the manufacturing chemist to solve the problems before him by purely chemical means, of some of which we may as little dream to-day as a few years ago it could

have been imagined that nickel would be extracted from its ores by means of carbon monoxide.

At a meeting of this Association which brings before us an entirely new form of energy, the Röntgen rays, which have enabled us to see through doors and walls, and to look inside the human body: which brings before us a new form of matter, represented by argon and helium, which, as their discoverers, Lord Rayleigh and Professor Ramsay, have now abundantly proved, are certainly elementary bodies, inasmuch as they cannot be split up further, but are not chemical elements, as they possess no chemical affinity and do not enter into combinations,—at a meeting at which such astounding and unexpected secrets of Nature are revealed to us, who would call in doubt that, notwithstanding the immense progress pure and applied science have made during this century, new and greater and farther-reaching discoveries are still in store for ages to come?

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ON THE
# AMOUNT OF GOLD AND SILVER IN SEA-WATER.[*]

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

(Concluded from p. 161).

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### Quantitative Tests.

UNFORTUNATELY all the samples had been used up in making qualitative tests for gold, but, in default of more water, the chlorine-water solutions and precipitates yielded by the stannous chloride from each batch of tests were mixed together and evaporated to dryness and then scorified and cupelled so as to determine the amount of gold. The assays were not done separately on each test, as it was thought that the gold beads, if any, would be too small to weigh.

*Southern Sea-waters.*—The first batch of tests, Nos. 1 to 6, *i.e.*, the extracts from six litres, gave 0·003 grain of gold, *i.e.*, 0·508 grain of gold per ton, or 0·38 grain per cubic yard, or 0·032 m.grm. per litre.

*Second Batch.*—The precipitate from twelve litres used for the second set of tests gave 0·009 grain, *i.e.*, 0·76 grain of gold per ton, or 0·57 grain per cubic yard, or 0·048 m.grm. per litre. The film was treated twice with chlorine water, and the two extracts added together.

*Third Batch.*—9·025 litres gave 0·0069 grain of gold, *i.e.*, 1·09 grain per ton, or 0·58 grain per cubic yard, or 0·049 m.grm. per litre.

### Northern Sea-waters.

8·100 litres gave 0·0060 grain of gold, equal to 0·75 grain per ton, or 0·56 grain per cubic yard, or 0·048 m.grm. per litre.

In calculating the amount of gold per ton or cubic yard, the specific gravity was in each case corrected to 1·026, *i.e.*, the mean results obtained by the *Challenger* Expedition, corrected to 15·5° C. for sea-water off the coast of New South Wales.

Before proceeding with further determinations of gold in sea-water, experiments were made to ascertain what loss of gold was sustained in the case of solutions containing known quantities of gold.

### Experiments with Distilled Water and Added Gold.

The following experiments were made to ascertain whether small quantities of gold in dilute solution could be recovered by treatment with ferrous sulphate and other reagents. After adding the ferrous sulphate the solution was exposed in large new shallow photographer's developing dishes for some days, so that the ferrous sulphate might be slowly oxidised and precipitated; in some

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[*] Read before the Royal Society of N. S. Wales.

cases glass cylinders were used and air blown through the solution. To complete the precipitation ammonia was added, the precipitate collected, washed, dried, scorified, and cupelled.

From the following results it will be seen that there was but little loss in some cases, but a good deal in others, partly due to imperfect precipitation by the ferrous sulphate, and partly to the loss during cupellation. In most cases the treatment with ferrous sulphate, oxidation and precipitation, was repeated upon the filtrate from the first precipitate.

1000 c.c. distilled water and 1 c.c. of 0·01 per cent $AuCl_3$ solution = 0·00154 grain gold.

1. Treated with 0·5 grm. $FeSO_4$ and $NH_3$
   yielded .. .... .. .. .. .. 0·0015 gr.
2. Filtrate treated with 0·25 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0000
                                   ————
   Gold = 0·0015 „

1000 c.c. distilled water (containing 30 grms. NaCl) and 1 c.c. of 0·01 per cent $AuCl_3$ solution = 0·0015 grain of gold.

1. Treated with 0·5 grm. $FeSO_4$ and $NH_3$
   yielded .. .. .. .. .. .. 0·0011 gr.
2. Filtrate treated with 0·25 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0000
                                   ————
   Gold = 0·0011 „

*I.e.,* a loss of 0·0004 grain of gold or 26·6 per cent. The presence of the NaCl seems to increase the loss of gold.

1000 c.c. distilled water and 100 c.c. of 0·01 per cent $AuCl_3$ solution = 0·1543 grain gold.

1. Treated with 1 grm. $FeSO_4$ and $NH_3$
   yielded .. .. .. .. .. .. 0·1253 gr.
2. Filtrate treated with 0·5 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0010 „
                                   ————
                                   0·1263 „

*I.e.,* a loss of 0·0280 grain gold or 18·14 per cent.

1000 c.c. distilled water and 100 c.c. of 0·01 per cent $AuCl_3$ solution = 0·1543 grain gold.

1. Treated with 1 grm. $FeSO_4$ and $NH_3$
   yielded .. .. .. .. .. .. 0·1327 gr.
2. Filtrate treated with 0·5 grm $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0010 „
                                   ————
                                   0·1337 „

*I.e.,* a loss of 0·0206 grain gold or 13·35 per cent.

### Experiments with Sea-water and Added Gold.

1000 c.c. Coogee sea-water and 100 c.c. of 0·01 per cent $AuCl_3$ solution = 0·1543 grain of added gold.

1. Treated with 0·5 grm. $FeSO_4$ and $NH_3$
   yielded .. .. .. .. .. .. 0·1430 gr.
2. Filtrate treated with 0·25 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0020 „
                                   ————
                                   0·1450 „

*I.e.,* a loss of 0·0093 grain of gold or 6·027 per cent.

1000 c.c. Coogee sea-water and 100 c.c. of 0·01 per cent $AuCl_3$ solution = 0·1543 grain gold.

1. Treated with 0·5 grm. $FeSO_4$ and $NH_3$
   yielded .. .. .. .. .. .. 0·1415 gr.
2. Filtrate treated with 0·25 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0020 „
                                   ————
                                   0·1435 „

*I.e.,* a loss of 0·0108 grain gold or 7 per cent.

500 c.c. Coogee sea-water and 10 c.c. of 0·01 per cent $AuCl_3$ solution = 0·0154 grain gold.

1. Treated with 1 grm. $FeSO_4$ and $NH_3$
   yielded .. .. .. .. .. .. 0·0095 gr.
2. Filtrate treated with 0·5 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0000
                                   ————
                                   0·0095 „

*I.e.,* a loss of 0·0059 grain gold or 38·31 per cent.

500 c.c. Coogee sea-water and 10 c.c. of 0·01 per cent $AuCl_3$ solution = 0·0154 grain gold.

1. Treated with barium chloride yielded 0·0013 gr.
2. Filtrate treated with 1 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. ·· 0·0069 „
                                   ————
                                   0·0082 „

*I.e.,* a loss of 0·0072 grain gold or 46·75 per cent.

2000 c.c. Coogee sea-water and 50 c.c. of 0·01 per cent $AuCl_3$ solution = 0·0771 grain gold.

1. Treated with 1 grm. lead acetate in
   acetic acid and precipitated by
   sheet zinc yielded .. .. .. .. 0·0708 gr.
2. Filtrate treated with 1 grm. $FeSO_4$
   and $NH_3$ yielded .. .. .. .. 0·0000
                                   ————
                                   0·0708 „

*I.e.,* a loss of 0·0063 grain gold or 8·17 per cent.

2000 c.c. Jervis Bay sea-water and 25 c.c. of 0·01 per cent $AuCl_3$ solution = 0·0385 grain gold.

1. Treated with 1 grm. lead acetate and
   precipitated by sheet zinc yielded 0·0235 gr.
2. Filtrate treated with 1 grm. $FeSO_4$
   snd $NH_3$ yielded .. .. .. .. 0·0016 „
                                   ————
                                   0·0251 „

*I.e.,* a loss of 0·0134 grain gold or 34·8 per cent.

It must be borne in mind that to the loss of gold sustained in the above experiments should be added the amount of gold also present in the sea-water. The smallest loss seems to be sustained when the gold is precipitated by ferrous sulphate and ammonia, but even that process is far from satisfactory.

### Additional Determinations of Gold in Sea-water from Coogee.

2000 c.c. treated with 0·5 grm. $FeSO_4$ and $NH_3$ yielded 0·0015 gr. = 0·76 grain per ton.

1. 9000 c.c. treated with 2·5
   grms. of $FeSO_4$, air
   blown through and
   $NH_3$ added, yielded .. 0·0028 gr. = 0·31 gr. per ton.
2. Filtrate treated with 1
   grm. $FeSO_4$ and $NH_3$
   added yielded .. .. 0·0035 gr. = 0·39 „   „
                       ————      ————
   Total.. .. 0·0063 gr. = 0·70 „   „

1. 2000 c.c. treated with 1
   grm. lead acetate and
   precipitated by sheet
   zinc yielded .. .. 0·0003 gr = 0·152 gr. per ton.
2. Filtrate treated with 1
   grm. $FeSO_4$ and $NH_3$
   yielded.. .. .. .. 0·0002 gr. = 0·101 „   „
                       ————      ————
   Total.. .. 0·0005 gr. = 0·253 „   „

It was found when large quantities of Coogee sea-water *e.g.,* 45 litres, were treated with from 1·5 to 5 grms. of ferrous sulphate, followed by exposure for oxidation, scorification, and cupellation, that the amount of gold

obtained was very much less in proportion than that yielded by treating one or two litres.

Several trials were made, a larger quantity of ferrous sulphate would doubtless have given results similar to those obtained from two litres; but I have not had time to repeat the experiments with large quantities of ferrous sulphate—as dealing with large quantities is slow and laborious with ordinary laboratory appliances.

The inside of the 36-gallon cask which had contained the Coogee sea-water was scraped, but very imperfectly, about two ounces of scrapings obtained; they were incinerated, scorified, and cupelled, when a bead was obtained containing—

0·0070 grain of silver = 5 dwt. 5·43 gr. per ton.
0·0017 „ gold = 1 „ 6·46 „

Only a part of the barrel was scraped, and that not deeply; but the above results are quite sufficient to show that the gold and silver in sea-water are precipitated by the wood, &c.; hence water which has been kept in wooden vessels does not yield the full amount of these metals, and the very small amount of silver found in sea-water by Malaguti may have been due to his keeping the sea-water in a wooden cistern.

All my experiments were made upon sea-water collected and kept in glass vessels, with the exception of the later ones on Coogee water, which had been kept in the barrel.

### Gold in Sea-water Collected off Jervis Bay.

1. 2000 c.c. treated with 1 grm. $FeSO_4$ yielded.. 0·0001 gr.=0·05 gr. per ton.
2. Filtrate treated with 0·5 grm. $FeSO_4$ and $NH_3$ yielded .. .. .. 0·0002 gr.=0·101 „ „

Total.. .. 0·0003    0·151 „ „

1. 2000 c.c. treated with 1 grm. lead acetate and precipitated by sheet zinc yielded .. .. 0·0020 gr.=1·016 gr. per ton.
2. Filtrate treated with 1 grm. $FeSO_4$ and $NH_3$ yielded .. .. .. 0·0000 gr.=0·000 „ „

Total.. .. 0·0020    1·016 „ „

1000 c.c. treated with chlorine, and then with 5 c.c. carbon disulphide, to dissolve out any iodine or bromine which might have been set free, decanted, 1 grm. lead acetate added, and precipitated by zinc, yielded 0·0005 gr. =0·508 gr. per ton.

1000 c.c. treated with 2 grms. of mercuric chloride for four days and then precipitated by $H_2S$, yielded 0·508 gr. gold per ton.

Experiments with other processes are now being carried out; but as they are not complete the results are deferred for a later paper.

To test the ordinary Sydney water supply, collected over a sandstone area, 124 lbs. weight of the laboratory tap-water was tested for silver and gold by adding 100 c.c. sulphurous acid, 5 grms. ferrous sulphate, and allowing to oxidise for several days; the iron hydroxide was then precipitated by ammonia, scorified, and cupelled, but neither gold nor silver was found.

The amount of gold obtained from sea-waters in the foregoing experiments must necessarily be less than the total amount of gold present in the water, since it was found that known quantities of gold chloride solution added to distilled and sea-waters and then estimated by precipitation, scorification, and cupellation nearly always showed a loss, and sometimes a very considerable one.

All the above evidence is in favour of gold being present in sea-water off the New South Wales coast in the proportion of about 0·5 to 1 grain per ton, or in round numbers from 130 to 260 tons of gold per cubic mile. This, of course, means an enormous amount for the whole of the ocean, the cubic contents of which used to be put down at 400,000,000 cubic miles; and if the gold be uniformly present at the rate of 1 grain per ton the total amount would be over 100,000,000,000 tons of gold; a later estimate is 308,710,679 cubic miles, this even would mean over 75,000,000,000 tons of gold. But at the present day it would probably not pay to extract the gold by itself, although it might as a by-product in the manufacture of salt, bromine, &c. The enormous amount of gold in the sea is, however, probably very small in comparison with the amount scattered through sedimentary and crystallised rocks, *i.e.*, apart from gold in veins and other deposits.

### Silver in Sea-water.

All the sea-waters gave some silver, usually from 1 to 2 grains per ton, but I consider the scorification and cupellation process lacking in the necessary precision for the exact determination of silver in such minute quantities as it exists in sea-water; I have therefore omitted all the determinations of silver from this paper, but I may publish them later on with the results of other experiments now in hand.

Malaguti estimated the amount of silver in sea-water at 0·001 grm. per 100 kilos. of sea-water, or at only 0·15 grains per ton; but I have quoted him more fully in a paper entitled " On the Removal of Gold and Silver from Sea-water by Muntz Metal Sheathing," which will appear in an early issue of this journal.

## ON THE FORM OF THE ATOMS,
### By C. FOURLINNIE.

WE have here a notice of a remarkable work extracted from the *Bulletin de la Société Chimique de Paris.*

The author endeavours to solve the following problem:— Can we explain the properties of the simple substances by admitting that their atoms are constituted of a unique and homogeneous substance having forms differing geometrically in each elementary body?

Limiting this research to the non-metals, the author reaches the conclusion that the non-metals arranged by Dumas in the same family possess atoms of the same form but of different dimensions, whilst the non-metals belonging to two different families have dissimilar atoms.

On carrying this analogy further, M. Fourlinnie shows that these atomic forms must be regular polyhedra; a conclusion perfectly in harmony with the fact that there can exist only five regular polyhedra corresponding to the five families of Dumas.

In order to effect this determination he has been led to compare the volumes of the different regular polyhedra, and he finds that the volumes of the hexahedron, the octahedron, the dodecahedron, and the icosohedron, inscribed in the same sphere, are relatively as the numbers 19, 16, 14, and 12, which are relatively the atomic weights of fluorine, oxygen, nitrogen, and carbon.

The author is then naturally led to conclude that the elements of the fluorine group have hexahedric atoms; those of the oxygen group, octahedric atoms; those of the nitrogen group, dodecahedric atoms; and those, lastly, of the carbon family, atoms having the form of regular icosohedra; whence, by exclusion, the regular tetrahedron belongs to hydrogen.

It further results that the simple bodies, the heads of the series F, O, N, C, have atoms possessing very distinctly the same apotheme, a circumstance which leads to the hope that we may, in accordance with the predictions of Schützenberger, fix the decimal divisions of the atomic weights by mathematical calculation.

After some interesting reflections on the attractive and repulsive actions of atoms, the author examines the consequence of his theory as regards atomicity and the combination of atoms among themselves.

When the atoms combine they take a state of stable equilibrium, where the axes—determined either by the surfaces (apothemes) or by the apices—coincide with each other.

By the aid of these considerations the double atomicity of oxygen is easily explained. It is the same with the triple atomicity of nitrogen; further, for this element the co-existence of the atomicities 3 and 5 meets with a striking appreciation. In the former case the equilibrium is determined by the apothemes, in the second by the apices.

For carbon the tetratomicity is more difficult; it necessitates an equilibrium, in part following the apothemes, and in part following the axes of the apices.

The ingenious theories of M. Fourlinnie are certainly not out of the reach of criticism. They recommend themselves to the favourable notice of the scientific world by their novelty and their originality.

They ought to be regarded as the germ of a new theory which may perhaps some day cast a novel light on the question of the mutual relations of the atomic weights.

It is, we believe, the first time that there has been given a relation of a mathematical order between the numerical values and the atomic weights of the elementary bodies fluorine, oxygen, nitrogen, carbon.

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## NOTE ON THE SOLUBILITY OF BISMUTH SULPHIDE IN SODIUM SULPHIDE,

### WITH SPECIAL REFERENCE TO

## THE ESTIMATION OF SMALL AMOUNTS OF BISMUTH IN ANTI-FRICTION ALLOYS.

### By THOMAS B. STILLMAN.

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THE method of separation of lead, copper, and bismuth from antimony, arsenic, and tin, by the use of sodium sulphide, is quite general. This is dependent upon the usually accepted statement that the sulphides of bismuth, lead, and copper are insoluble, and the sulphides of arsenic, antimony, and tin are soluble in sodium sulphide. This process of separation is employed in the analysis of various alloys, especially of anti-friction alloys, containing lead, tin, antimony, &c.

An alloy used for similar purposes, but containing, in addition to lead, copper, antimony, and tin, a very small amount of bismuth, was recently submitted to me for analysis.

After complete solution of the alloy in hydrochloric acid with a few drops of nitric acid, the acid was neutralised with sodium hydroxide, sodium sulphide solution (1·06 sp. gr.) added, and the heat applied for twenty minutes. The solution was filtered, and the filtrate examined for the antimony and tin with satisfactory results.

The precipitate of insoluble sulphides remaining upon the filter was found to contain lead and copper, but no bismuth. This indicated that the small amount of bismuth which was present in the alloy had gone into solution in the sodium sulphide.

To prove this theory, I weighed 0·128 grm. of pure bismuth nitrate, dissolved in 25 c.c. of water with a few drops of nitric acid, the clear solution neutralised with sodium hydroxide, 75 c.c. solution of sodium sulphide added, and warmed to a temperature near boiling for twenty minutes. The solution was filtered from the bismuth sulphide, remaining insoluble in the sodium sulphide. The clear filtrate was rendered faintly acid with hydrochloric acid, when a brownish black precipitate immediately formed. This precipitate was filtered, dissolved in hot nitric acid and evaporated to dryness, and ignited in a weighed porcelain crucible. The residue obtained was 0·031 grm. of bismuth trioxide, and strongly yellow in colour. It was dissolved in a few drops of hydrochloric acid, and the three following confirmatory tests for bismuth were made:—

1. A portion of the solution was poured into a large amount of water, forming immediately a white precipitate of bismuth oxychloride.

2. A portion was tested by Schneider's test, the most delicate test for bismuth, the reaction obtained being strong and characteristic.

3. A portion was diluted with water, not enough to cause precipitation, and the solution saturated with hydrogen sulphide. The precipitate formed was brownish-black in colour.

These three tests are absolutely confirmative of the presence of bismuth, and also show the absence of the other metals. By thus using pure bismuth nitrate for this test, lead, copper, antimony, and tin are not present.

If now an analyst should weigh 12 grms. of an alloy, composed approximately of lead 80 per cent, antimony 15 per cent, tin 4·75 per cent, and bismuth 0·25 per cent ("magnolia metal"), and sodium sulphide solution be used for the separation of the tin and antimony from the lead and bismuth, all of the bismuth present would pass into solution and escape determination by the analyst.

No analyst, however, would use as much as 12 grms. of such an alloy for analysis, but rather 1 or 2 grms.

If 1 grm. be taken and sodium sulphide used as above indicated, 3 per cent of bismuth might be present, and all of it pass into solution in the sodium sulphide instead of remaining as an insoluble sulphide with the lead sulphide. — *Journal of the American Chemical Society*, vol. xviii., No. 8, August, 1896.

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## LONDON WATER SUPPLY.

### REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1896.

#### By WILLIAM CROOKES, F.R.S.,
and
#### PROFESSOR DEWAR, F.R.S.

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*To* MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
*Water Examiner, Metropolis Water Act,* 1871.

London, September 12th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Aug. 1st to Aug. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined six were recorded as "clear but dull," the remainder being clear, bright, and well filtered.

We have again to record a deficiency of rainfall in the Thames Valley.

The average fall for the month is.. .. 2·32 inches
The actual fall at Oxford has been .. 2·01 „

Deficiency .. .. 0·31 „

Making the total deficiency for this year 5·97 inches.

On the other hand the quality of the water is of very high standard, as the following bacteriological results show:—

|  | Colonies per c.c. |
|---|---|
| Thames water, unfiltered .. .. .. .. .. | 1133 |
| Thames water, from the clear water wells of the five Thames-derived supplies.. highest | 43 |
| Ditto     ditto     .. .. .. .. lowest | 6 |
| Ditto     ditto     .. (12 samples) mean | 17 |
| New River water, unfiltered .. .. .. .. | 361 |
| New River water, from the Company's clear water well .. .. .. .. .. .. .. .. | 3 |
| River Lea water, unfiltered .. .. .. .. | 537 |
| River Lea water from the East London Company's clear water well .. .. .. .. .. | 5 |

The above results are confirmed by the chemical analysis.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

# THE INTRODUCTION OF STANDARD METHODS OF ANALYSIS.*

By the Baron HANNS JUPTNER VON JONSTORFF
(Neuberg, Austria).

(Concluded from p. 160).

As I also had frequently met with very considerable differences in the sulphur contents of the same sample of steel, I took from a cut piece of sheet iron, 30 millimetres broad and 6 millimetres thick, the high sulphur percentages of which permitted the weighing out of small samples, sixteen samples in the manner shown in Fig. 1, and with each two sulphur determinations were made so as to show that the differences were not due to the methods employed. The results were as follows:—

| XIII. | | IX. | | V. | | I. | |
|---|---|---|---|---|---|---|---|
| 0·058 0·048 | 0·053 | 0·053 0·060 | 0·056 | 0·095 0·090 | 0·093 | 0·092 0·092 | 0·092 |
| **XIV.** | | **X.** | | **VI.** | | **II.** | |
| 0·043 0·034 | 0·039 | 0·058 0·062 | 0·060 | 0·070 0·074 | 0·072 | 0·086 0·076 | 0·082 |
| **XV.** | | **XI.** | | **VII.** | | **III.** | |
| 0·057 0·049 | 0·053 | 0·042 0·035 | 0·038 | 0·075 0·085 | 0·080 | 0·095 0·098 | 0·097 |
| **XVI.** | | **XII.** | | **VIII.** | | **IV.** | |
| 0·042 0·032 | 0·037 | 0·080 0·090 | 0·085 | 0·075 0·088 | 0·082 | 0·053 0·053 | 0·053 |

The greatest difference between two pairs of determinations amounted to 0·013 per cent (sample viii.), and that at a place in which very varying sulphur contents adjoin each other (iii. with 0·097, iv. with 0·053, and xi. with 0·038 per cent of sulphur); whilst the maximum difference between all the sixteen mean analyses was 0·060.

The irregularity of the distribution is shown in Fig. 2.

In a large quantity of samples of filings irregularities in the composition of the material are exhibited by the differences in the analytical results. These are of so local a nature that they can only be detected under the microscope. The brittle parts of the material give finer filings than those which are more tough. The former must consequently collect at the bottom of the vessel that serves to receive the sample, more especially when it is violently stirred with the object of ensuring the best possible mixing.

A very interesting series of observations bearing on this point have been published by L. Schneider (*Oesterr. Zeit.*

* Read before the Iron and Steel Institute.

*für Berg- und Hüttenwesen*, 1894, p. 244). The only source of regret is that the two portions of the material were not analysed separately. The results are given in the Table.

In sample No. 13, the laminated portion contained 1·0 per cent of chromium, and the powder contained 0·7 per cent. The comminution of steel samples is effected by means of hammering. In the figures given in Columns 3 and 4 in Nos. 16 and 17, there appears to be a misprint in the original, as the total exceeds 100.

The behaviour is the same with graphitic grey pig-iron, especially in metal average analyses. Thus, I found (*Oesterreichische Zeitschrift fur Berg- und Huttenwesen*, 1890, p. 273) in an average sample of spiegeleisen, in nine determinations, variations in the manganese contents between 6·3 and 13·3 per cent, an observation which was confirmed by J. Kail (*Ibid.*, p. 506) for other elements.

To avoid these difficulties, not only must the irregular distribution of the elements in iron and steel materials be closely studied, but also some agreement must be arrived at as to the method of taking the samples. In this last connection I would like to submit the two following proposals:—

(a). *That it is best entirely to Exclude Average Samples of Metals.*—In the majority of cases it is much better to examine a number of separate samples, and to calculate the average from these results. Not only in this way may a satisfactory agreement be arrived at between the various samples, but a good idea is also obtained of the variations in composition of the material under investigation.

(b). *In the case of grey or mottled pig-iron*, in the determination of carbon, only so much of the metal should be broken down as is necessary for the test; that is to say, the whole of the powdered material is to be used up in the determination.

It is scarcely necessary to point out that all solutions used should be thoroughly mixed, whether these are solutions of the samples or standard solutions.

The detailed consideration of the sources of error in chemical analyses will have shown, even to non-chemists, that chemical analysis, especially that of steel, is by no means a simple matter, and that it is necessary to place it in the hands of skilled chemists if it is a question of obtaining accurate results. Is, however, such a degree of accuracy always necessary? To answer this question, the various uses to which analysis is put must be considered. One must distinguish between (1) analyses which are intended for use in controlling the work at the works; (2) trade analyses; (3) analyses which are to show the reason why the material under examination possesses certain properties, or whether it is suitable for certain definite purposes; (4) analyses connected with scientific investigations, where it is a question of ascertaining the constitution of iron materials, and the investigation of the relations existing between their chemical composition and their physical properties, &c.

For the purposes of works control, relative accuracy is adequate; that is to say, the method must not only show a plus or minus of the substance to be determined, but also with equal contents give good agreement, at least in all cases which may occur in the locality in question. It is desirable that these results should agree as nearly as possible with the true percentages, but this is a secondary matter as compared with the necessity of making as many as possible of these determinations simultaneously, and in the shortest time.

Such a method, for instance, is the well-known Eggertz colorimetric method for the determination of carbon. This gives results which are quite adequate for work control purposes in all cases where the material of the sample is produced under similar conditions as to hardening. Under no circumstances, however, can it be adopted if it is a question of the simultaneous examination of unhardened, hardened, and annealed steel, or of foreign steels whose methods of manufacture are not exactly known.

| No. | Steel. | Laminated residue. Per cent. | Pulverulent residue. Per cent. | Percentage composition. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C. | Si. | P. | S. | Mn. | Cu. | W. | Cr. | Ni. |
| 1. | Nickel steel .. .. .. .. .. | 99 | 1 | 0·42 | 0·22 | — | — | 0·22 | — | — | — | 6·0 |
| 2. | Filings from a foreign steel sample | 99 | 1 | 0·46 | 0·15 | 0·04 | 0·01 | 0·48 | 0·08 | — | — | — |
| 3. | Krupp tool steel .. .. .. .. | 98 | 2 | 0·90 | 0·28 | 0·02 | 0·01 | 0·26 | 0·05 | 0·11 | — | — |
| 4. | St. Egyd steel .. .. .. .. | 96 | 4 | 0·67 | 0·37 | 0·04 | 0·05 | 0·23 | — | — | — | — |
| 5. | St. Egyd steel .. .. .. .. | 92 | 8 | 1·20 | 0·35 | 0·02 | 0·03 | 0·23 | — | — | — | — |
| 6. | Puddled steel .. .. .. .. | 94 | 6 | 0·90 | 0·17 | 0·02 | 0·01 | 0·11 | — | — | — | — |
| 7. | Witkowitz steel *a* .. .. .. | 90 | 10 | 0·15 | ? | — | — | — | — | — | — | — |
| 8. | Witkowitz steel *b* .. .. .. | 90 | 10 | 0·08 | ? | — | — | — | — | — | — | — |
| 9. | Chrome steel .. .. .. .. | 90 | 10 | ? | — | — | — | — | — | — | 0·95 | — |
| 10. | Zeltweg steel .. .. .. .. | 90 | 10 | 0·30 | 0·02 | 0·09 | ? | 0·20 | — | — | — | — |
| 11. | Neuberg steel .. .. .. .. | 90 | 10 | 0·52 | 0·36 | 0·15 | 0·06 | 0·39 | 0·18 | — | — | — |
| 12. | Open-hearth steel from Donawitz | 89 | 11 | 0·20 | 0·04 | 0·08 | ? | 0·13 | — | — | — | — |
| 13. | Chrome steel .. .. .. .. | 85 | 15 | 1·45 | 0·31 | 0·01 | 0·02 | 0·42 | 0·03 | — | 1·00 | — |
| 14. | Neuberg steel .. .. .. .. | 78 | 22 | 0·56 | 0·44 | 0·08 | 0·05 | 0·47 | 0·10 | — | — | — |
| 15. | Riffle steel .. .. .. .. .. | 78 | 22 | 1·24 | 0·81 | 0·02 | 0·02 | 0·21 | — | 1·90 | — | — |
| 16. | Open-hearth steel *a* .. .. .. | 69 | 32 | 0·13 | 0·02 | 0·08 | 0·04 | 0·47 | 0·03 | — | — | — |
| 17. | Open-hearth steel *b* .. .. .. | 68 | 40 | 0·14 | 0·02 | 0·07 | 0·03 | 0·17 | 0·01 | — | — | — |
| 18. | Eibiswald puddled steel .. .. | 66 | 34 | 0·90 | 0·08 | 0·02 | 0·02 | 0·13 | — | — | — | — |
| 19. | Tungsten steel from Kapfenburg | 60 | 40 | 2·07 | 0·70 | 0·03 | 0·01 | 0·54 | 0·01 | 6·13 | — | — |
| 20. | Böhler tool steel.. .. .. .. | 50 | 50 | 1·20 | 0·20 | 0·03 | 0·02 | 0·12 | — | — | — | — |
| 21. | Crucible steel .. .. .. .. | 32 | 68 | 0·83 | 0·08 | 0·03 | 0·02 | 0·31 | 0·04 | — | 2·50 | — |
| 22. | Neuberg tungsten steel .. .. | 5 | 95 | 2·60 | 0·34 | ? | 0·01 | ? | 0·01 | 6·40 | 0·10 | — |
| 23. | Musket steel.. .. .. .. .. | 0 | 100 | 2·24 | 0·99 | 0·04 | 0·02 | 1·56 | tr. | 6·26 | 0·22 | — |
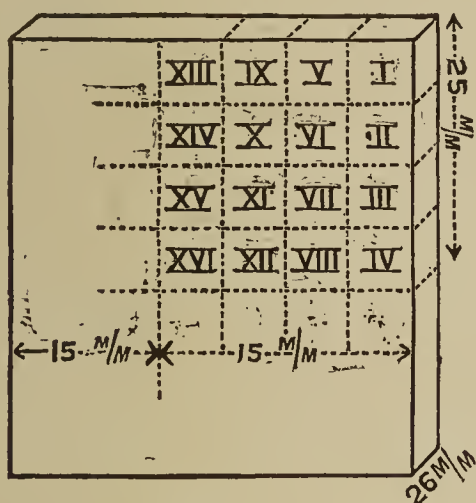


FIG. I.
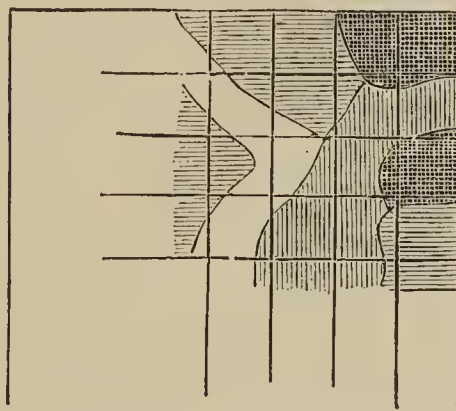


☐ UNDER — 0·05 PER CENT OF SULPHUR

▤ 0·05 — 0·065 % S

▥ 0·065 — 0·085 % S

▦ ABOVE — 0·085 % S

FIG 2

A second example is the phosphorus determination by the molybdate method by the aid of the rotation apparatus. It gives results which are perfectly satisfactory if all conditions as to its use are *exactly* complied with, and the point taken into consideration that the calculation factor varies with the volume of the precipitate. It follows that this method can be well recommended not only for works control purposes, but generally. Yet by slight variations in the manipulation the method gives differences which are so great that it can only be entrusted to trustworthy hands, even if it is only a question of works control analyses.

In the case of commercial analyses, to which also those analyses belong that are intended to ensure that the percentage limits of chemical composition required by contract are maintained, it is only possible to be content with this kind of requirement when both parties, the buyers and the sellers, have agreed to some method for the determination of each particular substance. Under certain conditions, therefore, it is possible to rest satisfied with *relative accuracy* even in trade analyses; but, as a general rule, it is best to aim at the highest possible degree of accuracy.

The question is quite different in the instances given under (3) and (4). Here the requirement of endeavouring to attain a maximum degree of accuracy takes the foremost place, while the possibility of making many determinations rapidly and at the same time is not so important.

It is therefore necessary to distinguish between—(*a*). *Methods for works control*, and, under certain circumstances, for trade purposes; and (*b*). *Methods for all other purposes*. With regard to these latter, I should like to draw attention to one other circumstance. Modern methods of analysis, such as are actually employed daily in practice, are, with almost the single exception of the determination of graphite, complete analyses. Iron materials are, however, in no way homogeneous substances such as minerals, but are mixtures of various compounds, analogous, that is, to rocks composed of several minerals, and there can be no question but that many samples of iron of quite identical elementary composition, according to the kind and quality of their inner components, may show altogether different physical properties. It has so far only been attempted to explain this in a few cases. At the present time the different forms of carbon are more intimately known, but practical methods for their determination suitable for use in the technical laboratories are wanting. With reference to certain other elements, phosphorus (L. Schneider, *Oesterreichische Zeitschrift für*

*Berg- und Hüttenwesen,* 1886, p. 736 ; H. von Jüptner, *Ibid.,* 1894, p. 209), chromium (H. Behrens and Van Linge, *Fresenius's Zeitschrift,* xxxiii., p. 573 ; H. von Jüptner, *Oesterr. Zeit. f. Berg- und Huttenwesen,* 1896, No. 2), tungsten (L. Schneider, *Oesterr. Zeit.,* 1895, No. 18), and others, some information has been given, but the notes referred to are very isolated in character, and consequently require confirmation by numerous investigations before general conclusions can be drawn from them. We know that all elements which can be precipitated by sulphuretted hydrogen are completely contained in the residue insoluble in dilute sulphuric acid (F. G. Müller, *Stahl und Eisen,* 1888, p. 293 ; Reinhardt, *Ibid.,* 1889, p. 405 ; von Reis, *Ibid.,* 1889, p. 720) ; that copper separates out in the iron mass in the form of metallic shots or as sulphide ; that phosphorus is partly evolved in the form of phosphuretted hydrogen by dilute acids, but that it in part remains undissolved (H. von Jüptner, *Oesterr. Zeit. f. Berg- und Huttenwesen,* 1894, p.208) as iron phosphide or manganese phosphide, $Fe_3P$ or $Mn_3P_2$; that slag is included in the metal, &c., &c.

It is just these kinds of investigations, however, which are of especial value, not only from a scientific point of view, but to an eminent degree for technical practice ; for it is only when a more accurate knowledge is obtained of the inner constitution of the varieties of iron met with in practice—and methods are known by which in every case this may be readily and accurately determined—that it will be possible to choose for every purpose a material of proper chemical composition and mechanical treatment, and to find means and ways in order to prepare it with certainty for every case. In this connection not only must chemical examination be adopted, but microscopic as well, a method which so far does not receive nearly the amount of attention it deserves.

In view of what has just been discussed, the questions to be considered—as I showed at the recent International Conference for the Unification of Testing Methods at Zürich—may in their general scope be briefly sketched out as follows :—There require to be studied—(1) The irregular character of the samples, and some agreement as to the method of taking the samples, must be arrived at, both as regards these irregularities and also any impurities introduced in the course of their being broken down to size. (2) At least all the more important methods of determination for all the constituents met with in iron and steel materials, including slag and gas inclusions, should be thoroughly studied and compared with one another, taking into consideration all possible sources of error. We can then either rest satisfied with this comparison or pass to the setting up of standard methods. In any case, it will be necessary to distinguish between methods for the works control, &c., in which, in the first instance, rapidity of completion has to be considered, and which may be defined as works assays, and the analytical methods required for every other purpose in which accuracy is the main requirement. (3) We must not confine ourselves to determinations of the various elements, but must direct our attention to such matters as permit of the various forms and combinations in which the several constituents can occur in technical varieties of iron, being distinguished and quantitatively determined.

In view of all that has been said above, it follows that the scope of the necessary inquiry is of an extremely wide character. It is so wide indeed that it is scarcely desirable to attempt the solution at the same time of all the questions requiring consideration. It would be better perhaps, to endeavour to solve these one after the other, and to rest contented at first with the following :—(1) Investigations relating to the want of homogeneity in the samples, and to some decision as to the method of sampling ; (2) examining the methods for the determination of the main constituents—that is to say, of carbon, silicon, manganese, sulphur, phosphorus, copper, and slag. (3) Since, moreover, as has been pointed out, the value of the atomic weights on which the analytical calculations are based have at least in certain cases considerable influence on the results, it is desirable to arrive at either an agreement, perhaps temporary in character, as to the values to be adopted, or else to revise the atomic weights necessary in connection with the methods under examination.

To arrive at a general agreement of the methods to be examined, it would appear desirable, from the very commencement, to lay down definitely the general principles which are to be adopted. Much that has to do with this has been already shown, so that I may confine myself to a few brief remarks on this point.

It must not be forgotten that we have to consider in the first instance, practical work, and that even for our scientific purposes, which we also wish to place at the service of practical work, very tedious or troublesome methods have no value, or at most but very little. In this case, too, it is usually not so much the question of a single analysis, as of analytical material wide in scope that has to be the basis for further study.

But even for theoretical purposes, other conditions being equal, simple methods appear more desirable than more complicated ones, for every operation introduces sources of error ; the greater the number of operations necessary and the longer these take, the greater both in number and in degree are the errors to which the analyst is exposed.

Permit me to give an example. The following method for the determination of phosphorus was proposed :— The phosphorus is to be precipitated from a nitric acid solution as ammonium phosphomolybdate, the precipitate collected on a filter, dissolved, precipitated with magnesia mixture, filtered, again dissolved, and finally titrated with uranium acetate. Why was not the phosphomolybdate, or at least the magnesia precipitate, weighed direct ?

That we have to distinguish between works assays and precise analytical methods has been already pointed out. It is naturally advantageous, however, for a method to possess at the same time both the valuable properties of assay methods and of scientific methods, and consequently to be suited to both purposes.

It must not be forgotten that skill, personal factors, exceptional or other circumstances, may cause one analyst to prefer one method and another a second. This is a circumstance which it seems to me should be considered, to reduce personal errors to a minimum, and I should therefore consider it desirable that for every element many methods, based on as widely differing facts as possible, should be tested, and both their relative and their absolute accuracy ascertained.

It may here be pointed out that it can be by no means our aim to arrange normal methods, which are to be used always, under all conditions, and at all times. On the contrary, it must be left to every chemist to work as he thinks best, and the progress which scientific knowledge is making must also be taken into consideration—a progress that now-a-days is enormous. On the other hand, as has been pointed out, our aim must be to arrange for as many different methods as possible, and to ascertain their relative conditions of value. These methods are to serve as standard methods in investigating the particular method used by any individual analyst, or new methods, and are always to be used when differences in the results of analyses made at different laboratories have to be explained. But to be in accord with scientific progress, any other methods which may from time to time be proposed must be all included in the scope of the investigations.

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Sources of Error in Alkalimetry.—Fr. Scheiding (*Zeit. f. Angewandte Chemie*).—The author lays especial weight on the influence of carbonic acid. He considers it fallacious to allow lye to stand for hours in an open bottle and then afterwards execute titrations in the cold, using phenolphthalein as indicator.

## NOTICES OF BOOKS.

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*A Systematic Handbook of Volumetric Analysis; or, the 'Quantitative Estimation of Chemical Substances by Measure applied to Liquids, Solids, and Gases.* Adapted to the requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, &c., and for the Calculation of Substances used in Commerce, Agriculture, and the Arts. By FRANCIS SUTTON, F.I.C., F.C.S., Public Analyst for the County of Norfolk. Seventh Edition, Enlarged and Improved. London: J. and A. Churchill. 1896. Pp. 587.

"SUTTON'S Volumetric Analysis" has been for more than thirty years an indispensable laboratory companion, and has been regularly enlarged and improved in accordance with the extension of volumetric methods. This will be at once seen on comparing the first edition with the work as it now appears. In the earlier editions gas-analysis was overlooked—being, in fact, almost unknown. The analysis of water consisted simply of the Clarke method for the determination of its hardness, the estimation of nitrogen not being attempted either by the Frankland, the Wanklyn, or the Kjeldahl methods, which were in those days non-existent. We now find a microscopic examination recommended, not in the place of chemical analysis, but as a useful adjunct. The biological procedures are scarcely noticed. The Frankland and Armstrong method receives a more extended notice than in some of the earlier editions; and, on the other hand, less space is devoted to the Wanklyn and Chapman application of the Nessler reaction. The determination of the oxygen existing in solution in waters is duly noticed as regards its application to polluted waters. It will be remarked, however, that the names of Wanklyn, Dewar, and Tidy do not occur in the index.

The chapter on indicators is very valuable, and includes the latest observations, such as those of Mylius and Förster.

We are correctly informed that in gas-analysis the apparatus of Scheibler is practically superseded.

We cannot congratulate the author on having retained the term "indigo-carmine," a solecism as painful as that of the modern draper and modiste when they call a bluish grey shade "gobelin."

Full instructions are given for the detection of phosphoric acid in water.

A paragraph is given on reporting the results of water analysis—the joint opinion of special committees of the British and the American Associations. The report is to be found in full in the CHEMICAL NEWS (vol. lx., pp. 203, 204).

Without any further examination, we may safely say that it is a book with which every laboratory ought to be furnished.

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*Elementary Quantitative Chemical Analysis.* Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., F.I.C., Professor of Chemistry in the South-West London Polytechnic. London: J. and A. Churchill. 1896. Pp. 238.

THIS book is divided into sections, treating successively of general processes, gravimetric analysis, volumetric analysis, of the analysis of complex substances, of gas-analysis, and including tables of reference.

The various processes will be found to be carefully and clearly described, and may be followed with confidence. Among the complex substances examined we find no mention of water further than the determination of its "hardness."

The apparatus described for the volumetric determination of gases are those of Hempel and Lunge.

Among the typical results of analysis we find the composition of Nottingham coal-gas. It appears to be absolutely free from carbonic acid and from sulphur compounds, but is contaminated with 6·6 per cent carbon monoxide.

In the table of the elements argon and helium are absent, glucinum figures under the name beryllium, and didymium is retained in preference to its components neodymium and praseodymium.

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*The Book of the Dairy:* a Manual of the Science and Practice of Dairy Work. Translated from the German of W. FLEISCHMANN, Ph.D., Professor of Agriculture, and Director of the Agricultural Institute, Konigsberg University, Prussia, Honorary Member of the Royal Agricultural Society of England. By C. M. AIKMAN, M.A., Sc.D., F.R.S.E., F.I.C., and R. P. WRIGHT, F.H.A.S., F.R.S. Edin. London, Glasgow, and Dublin: Blackie and Son, Lim. 1896. 8vo., pp. 344.

Two facts cited in the translator's preface show that the British dairyman requires further instruction in his business. An income of £32,000,000 is derived from the sale of dairy produce at home, or one-sixth of the whole income of British agriculture. Yet we import from the Continent butter and cheese to the annual value of more than £20,000,000. Hence we have still vast room for improvement! This must especially be admitted if it is considered that our climate is admirably adapted for grazing purposes, whilst land fit for pasturage is lying waste and idle. Hence one of the most important remedies for the present agricultural depression is the diffusion of practical knowledge on the production of butter and cheese, and its general adoption. According to the author, and according to actual facts, we have in this country most to learn from Swiss practice; little, if anything, to learn from Belgium, as the odour of Limburg cheese has long been a standing joke. It is not gratifying to learn that the Dutch "Edam" cheese is largely exported to Australia. Some Dutch cheeses, like those of Suffolk, are almost hard enough for use as projectiles.

From German practice little is to be learnt on the preparation of cheese and butter. But Prof. Fleischmann has carefully studied and collated the methods of the countries and the special districts where dairying is carried on most successfully, comparing the procedures employed with the produce obtained, and is thus successful in giving most valuable advice to the dairyman.

As in all other works on the composition of milk, we have found nothing either to confirm or to refute the empirical notion that the milk of short-horn cows is decidedly poorer than that of the long-horn's of Lancashire and the West Riding. Dr. Vieth's analysis, here quoted, shows that the milk of short-horns is poorer than that of the Jersey breed, though not to the traditional extent.

The employment of milch-cows as beasts of draught or burden is rightly condemned, but it is not common in Britain. The author's strictures on dishorning cattle are not endorsed by the translators, who contend—in our opinion with justice—that it is really humane to the cattle, and removes a source of danger to the attendants. We may here remark that in countries free from wolves, &c., pugnacious bulls should not be used for breeding.

The illustrations with which the book is enriched are very appropriate.

We remark with regret that although Ireland is naturally better adapted for dairying industries than England or Scotland, yet Irish cheese does not figure in the market, and that Irish butters are being more and more displaced by Continental produce. Why is this?

# CORRESPONDENCE.

## THE SCIENCE AND ART DEPARTMENT.

### *To the Editor of the Chemical News.*

SIR,—When some months ago it was rumoured that the Science and Art Department intended to modify their system of payments, and to abolish " payment on results," many of us rejoiced, and felt that at last there was some chance that the examination incubus which was smothering scientific teaching throughout the country would be removed. Alas! the regulations contained in the new edition of the " Science Directory " just published show that, so far from being relaxed, the cords of examinationism are to be drawn tighter than ever.

The payments under the new system are to take the form of attendance grants, at so much per head per attendance, the amount varying according to the efficiency of the teaching as measured by the report of the Inspector and *the success of the class at the May examinations*. No hint is given as to the relative importance which will be attached to the two factors. So it will be seen that there is still payment on results, though on a different and far less satisfactory—because less open —system.

Other regulations, now introduced for the first time, are very much worse, educationally, than any previously in force. Classes are to be in three stages (Elementary, Advanced, and Honours), but the new regulations as to payment apply only to the first two. These classes may not be taught together, and no student is to be admitted to an advanced class till he has passed the Science and Art Department Examination in the elementary stage.

These regulations destroy all trace of freedom in teaching. Hitherto a teacher has been to some extent free to teach on the lines he thought best, and to send his students up for examination, trusting to their being able to pass the examinations, and they were free to take either the elementary or advanced paper as they thought fit. This is no longer possible. No subject can be taught as a whole, but must be broken up into stages,—not according to any natural division of the subject or the judgment of the teacher, but according to the arbitrarily arranged syllabus of the Department, and the fitness of a student to pass from one stage to another is to be judged entirely by his success or failure in the Science and Art Department Examinations.

Under the old regulations good students often took the Advanced or sometimes even its Honours paper after one session of instruction in a class. Now that is not to be allowed. However well a student may be prepared, however much time he may give to study, however many hours per week may be given to teaching in the class, he will still have to go up for the Elementary Examination. This, I venture to say, the best students will not do.

In addition, there are regulations which will necessarily tend to the shortening of all lessons to the minimum of one hour for lectures, and one and a half hour—a ridiculously inadequate time—for laboratory instruction, and vexatious and troublesome rules as to the keeping of the class registers.

On the whole the new regulations are decidedly retrograde, and must still further lower the standard of teaching under the Department, and bring more discredit on to the whole system.

The way in which the changes have been made is also most unjust. The circular notifying them was sent out after many institutions had made and published their arrangements for the coming session, and the Directory containing the details has only just been issued after many classes have commenced work.

Surely for such serious changes ample notice should have been given.

The whole of the changes, in common with many of the existing regulations, seem based on the assumption that teachers are ignorant, incompetent, and dishonest, and that knowledge of science and how it should be taught is only to be found in the officials at South Kensington.—I am, &c.,

S.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxxiii., No. 10, September 7, 1896.

The inauguration of the statues erected to Pasteur, Florian, and the Abbé de Sauvages at Alais were arranged to take place on September 26th and 27th.

**Discharge of Electrised Bodies by the X Rays.**—Emilio Villari.—Will be inserted in full.

**Emission of the X Rays.**—Ch. E. Guillaume.—The law of emission as a function of the angle is not peculiar to the X rays ; we arrive at analogous relations in the case of ordinary light whenever it emanates from a body sufficiently transparent. The law of the cosine ceases to be true whenever for the *surface* of emission there is substituted a volume of emission of finite thickness.

### No. 11, September 14, 1896.

**Simultaneous Presence of Laccase and of Tyrosinase in the Juice of certain Fungi.**—G. Bertrand.—From one and the same juice extracted from certain fungi we may obtain on the one hand a liquid very rich in laccase, but without action on the tyrosin, and, on the other hand, a solution which scarcely shows the reactions of this soluble ferment, but possessing those of tyrosinase.

*Revue Universelle des Mines et de la Metallurgie.* Series 3, Vol. xxxv., No. 1.

This number contains no chemical matter.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 5, Vol. i., No. 8.

**Researches on the Structure of Metals, its Genesis, and its Transformations.**—Prof. Roberts-Austen and F. Osmond.—This memoir is from English sources.

# MISCELLANEOUS.

**National Value of Chemistry.**—It is fair to hold that the country that has the best chemists will, in the long run, be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best manufactured materials, the fewest wastes and unutilised forms of matters, the best guns, the strongest explosives, the most resistant armour. Its inhabitants will make the best use of their country's resources ; they will be the most healthy, the most free from disease ; they will oppose the least resistance to favourable evolution ; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition to-day between nations is essentially a competition in the science and applications of chemistry.—*North American Review.*

# TO CORRESPONDENTS.

H. L.—We can suggest no better or safer way than to sterilise the mixture by heat.

ERRATUM.—P. 76, col. 2, line 30 from bottom, *for* "0·19" *read* "0·019."

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1924.

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## MEASUREMENT OF ELECTRIC CURRENTS THROUGH AIR AT DIFFERENT DENSITIES DOWN TO ONE FIVE-MILLIONTH OF THE DENSITY OF ORDINARY AIR.[*]

### By Lord KELVIN, J. T. BOTTOMLEY, and MAGNUS MACLEAN.

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THE apparatus used in these experiments consisted of—
(1) A cylindrical tube 13 c.m. long and $1\frac{1}{2}$ c.m. diameter, with two aluminium wires as terminals ground to points 1·5 c.m. apart; (2) a large Wimshurst electrostatic machine of 24 plates; (3) a high-resistance mirror galvanometer to measure the current between the aluminium-point terminals inside the tube; (4) an electrostatic voltmeter to measure the difference of potential between the terminals of the tube; (5) a five-fall Sprengel pump, by means of which the density of the air inside the tube could be reduced to any desired extent. The galvanometer was placed on a block of paraffin between one terminal of the electric machine and one terminal of the glass tube. Its deflections were read by a telescope and its sensibility was arranged by external magnets, so that one division of deflection corresponded to 0·3 mikroampère. Our method of experimenting was to keep the density of the air constant while we varied the difference of potential between the terminals of the tube, and taking simultaneous readings on the voltmeter and on the galvanometer. The electric potential was varied either by varying the speed of rotation of the machine or by varying the distance between the needle-point terminals of the machine, or by a combination of both.

We found that at ordinary atmospheric density it requires a difference of potential of between 2000 and 3000 volts at the terminals of the tube before the galvanometer indicates any current. As the difference of potential is now increased, the current through the galvanometer increases at a greater ratio, so that if a curve be drawn with differences of potential as abscissæ and galvanometer readings or currents as ordinates, the curve is always concave towards the axis of current. Through this particular tube the currents at 3000, 5000, and 8000 volts difference of potential were 7·2, 17·6, and 63·2 mikroampère respectively. As the density of the air was diminished, the difference of potential necessary to start a current, as indicated by the galvanometer, gradually diminished also, till, at a density of about $\frac{1}{1000}$ of the ordinary density, a few score volts were sufficient to start a current. For the same difference of potential the current increased as the density of the air diminished; or otherwise, the same current was obtained by smaller differences of potential as the density of the air was reduced. Thus a current of about 50 mikroampère was obtained by differences of potential of 7400, 1090, 700, 370, 405, 570 volts, when the densities of the air were 1 (ordinary density), 0·058, 0·0093, 0·0007, 0·00006, 0·000024 respectively; or otherwise, when the air pressures were 750, 44, 7, $\frac{1}{2}$, $\frac{1}{22}$, $\frac{1}{55}$, m.m. of mercury respectively.

As the air density was still further reduced, the difference of potential necessary to start a current increased, and the current for the same difference of potential diminished. Thus, when the density of the air was reduced to one five-millionth of the density of air at ordinary atmospheric pressure and temperature, differ-

ences of potential of 3000, 5000, and 8000 volts gave currents of 1·3, 4·4, and 14·6 mikroampère respectively.

If a curve be drawn for a constant difference of potential, with air densities as abscissæ and currents as ordinates, we find the curve rising as the air density is diminished to about $\frac{1}{1000}$ or $\frac{1}{1500}$ of ordinary density; then falling again as the density is still further reduced to about a five-millionth of ordinary density. This is the lowest density we have experimented with, but we have no reason to doubt that at very much lower densities we would still be able to get measurable currents through the tube.

We are now experimenting with a tube 13 c.m. long and $1\frac{1}{2}$ c.m. diameter, having ball terminals of $\frac{1}{2}$ c.m. diameter and about 2 m.m. apart. The investigation is not complete enough for publishing any results.

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## CHEMICAL EDUCATION IN ENGLAND AND GERMANY.[*]

### By Sir HENRY ROSCOE.

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THE question as to how far the scientific, and especially the chemical, education in Germany is superior to that in England, and how far that superiority has influenced the German chemical industries as against our own, is one which at the present moment has come into prominence in the public prints. As the question of scientific education is one which the section has for some time past considered, it cannot be inappropriate at the present moment to introduce a discussion on this subject from a scientific point of view. That in Germany the appreciation of the national value of a high scientific education is greater than it is at the present day in England is a universally admitted fact. In that country we find Government institutions of every kind for the advancement of the highest scientific instruction in all branches; and Englishmen have not been slow to avail themselves of the generosity of the German nation in studying in that country under conditions and at a cost which their native land does not afford them. And the question, then, may well be asked, has the admitted want of this largely-developed higher scientific instruction in England been detrimental to the prosperity and progress of chemical industry in this country? And, on the other hand, has the existence of this facility in Germany fostered chemical manufactures and trades in that country? If this is so, as many believe, the point to enquire is in what way can we in England be placed in a position successfully to compete with Germany.

Although I am not one of those who take a pessimistic view of our national industries, chemical or otherwise, I have no doubt that many of the complaints which we hear are well founded.

In the opinion of some who have favoured the public with their views, the evil is to be found in the want of appreciation of science and of original research on the part of the manufacturers. If, say they, our manufacturers were as fully aware of the importance of the assistance which scientific investigation gives to their industries as are our German competitors, England would be well able to furnish educated men qualified for the work. Others, again, take a more general view, and see the origin of the difficulty in the system of university education, especially in our older seats of learning, where science teaching is not given free scope, and where too great a weight is laid on examinational results, and little encouragement given to original scientific investigation. And those who take this view further insist that if science found its legitimate expression in the university curriculum and available honours, schools would not be slow to take up the matter

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and to see that *their* instruction was made to lead up to university requirements, and thus the general scientific instruction in the country would be improved.

Both of these causes are probably at work in preventing that direct application of chemical research to industry, upon which alone its future success must depend. As an instance of this want of appreciation on the part of manufacturers and capitalists, I may remind the section that the initiation, from both its theoretical and practical side, of the great colour industry took place in this country. Not only was the first of these colours discovered by an Englishman, not only were all the raw materials required to be had in quantity in England—and nowhere else,—but the scientific men who have since been the means of inaugurating and carrying out in Germany this enormous industry were, at the inception of that industry, actually resident in Lancashire, and carried to Germany the practical results of their knowledge of English manufacturing methods, at that time scarcely known in their own country; and there is no reason in the nature of things why Caro, Martius, and Pauli, men who have since made their name illustrious in connection with German industries, should not, like our distinguished President of the Section, have remained in England to found here the industries which have brought millions into the revenues of Germany. What was it that prevented them ? Simply the want of foresight and of scientific knowledge and zeal among the English chemical manufacturers and capitalists of that time. If these men had been able to obtain financial support in Lancashire some thirty or forty years ago, the colour manufacture would have been a Lancashire instead of a German industry. Have we improved matters since that date ? Are our capitalists any more ready than they were to acknowledge the dependence of industry on science, and to take steps in advance in new directions ? Are our chemical industries on the wane, and must we in all departments yield the palm to Germany. The interesting address of our president has proved that this is not the case, and the success which has attended his labours and that of the able men with whom he is surrounded in his work is a signal example of what can be done in this country in opening out new paths. Another instance of this kind, also mentioned by him, is one which points in the same direction. The matters to which I refer are new departures due mainly to the scientific and practical genius of my friend Mr. Castner. It is almost a startling fact that sodium, which a few years ago was a chemical rarity, is now made by Davy's original electrolytic process, to the amount of five tons per week in one single works; that sodium peroxide, a body scarcely ever seen, even in the chemical laboratory, is also manufactured by scores of tons. Moreover, that electricity, which is every day becoming more and more the handmaid of the chemist, so that instead of our wandering to Section A, we compel that section to come to us, electricity, I say, is now called into requisition to manufacture two of the most common articles—caustic soda and bleaching powder. In both of these instances no difficulty has been found in obtaining requisite financial support, and in these instances England has led the way. And not only does America follow the lead, but the great firm of Solvay, which has always been the first to encourage and develope new applications of science to industry, has accepted this English invention as being one full of promise for the future. These instances, then, serve to show in the first place that there are people in England capable of originating discoveries, and also persons who are willing to give the financial support for the foundation of industries dependent on those discoveries.

But more than this, I maintain that with the single exception of colour manufacture, English chemists and English capitalists have in the past taken the lead in every branch of chemical industry. Our President's Address proved this up to the hilt in the case of chlorine. From the hour when Davy, in 1810, gave the proof of the

true character of this gas, and even before that, up to the present day, the only names, with the exception of Berthollet and Le Blanc, mentioned in the address are those of Englishmen—Tennant, Gossage, Muspratt, Dunlop, Weldon, and Deacon—are the men who made the real permanent advances in the industry of chlorine. In the cognate branch of the soda industry Le Blanc certainly claims the first place. But it is to Englishmen that the lasting success of Le Blanc's process is due; for without Glover's towers, Shank's lixiviating vats, and Chance's sulphur recovery process—and I might mention many others—the application of the great Frenchman's discovery must long ago have died a natural death; and these, and these alone, keep it now alive. Nor must we forget that, whilst the success of the ammonia-soda process is greatly due to Solvay, not only was the reaction given by two Englishmen—Dyer and Hemming, in 1838, —but the working out of the details of the process was accomplished on English soil by our President, who, from his long residence amongst us, and from the great work which during that time he has accomplished, we may claim—and I trust he will not be displeased—to be our countryman.

In other more general respects English chemical industry is to the fore. Our Society of Chemical Industry, founded fifteen years ago in this district, is the largest and most active in the world, and our journal is acknowledged both at home and abroad to be the best in existence.

But though we may justly point with pride to the work which has been done, and which is still being done, in this country in establishing chemical industries, it must be admitted that much remains to be done if we are to keep pace with the progress visible elsewhere.

What is needed is a more general appreciation of the value of high scientific education by our manufacturers and leaders of industry. It is true that things are improving, and in proof of this I may state that many of my former students at Owens College occupy now places of trust and importance in various departments of chemical industry. But the demand for highly educated men is still small. It has been said that manufacturers can buy the scientific aid which they need : of course they can. What we as teachers and as chemists have to deplore is that, as a rule, they do not buy it ; or, at least, they offer but a poor price for the article. In Germany a young man devotes six or seven years of his university course to the study of chemistry, because he knows that there is a good prospect of his obtaining a remunerative position afterwards. At the celebrated colour works at Höchst, near Frankfort, my friend Dr. Pauli has somewhere about a hundred well-educated university men working at research or conducting the various departments of his business, and these receive salaries ranging from £250 to £500 per annum ; and you may be sure that the directors at Höchst do not pay these salaries without getting a very good return for their money.

Our English laboratories and our English professors are as fully competent to turn out a finished article as are our German friends ; but if the article is not in demand there is not much inducement to manufacture it. Then, again, the raw material must be good, and it is an unfortunate fact that in this respect the Germans excel us. They have a recognised national system of secondary education : we have none. The students entering at a German university have gone through a severe and prolonged school education. Those coming to our colleges to be made chemists are too often innocent of anything that can be with truth termed secondary education. To remedy this evil, to " organise our secondary education," is the first step towards attaining the position which the higher scientific education occupies in Germany. It is to be hoped that the recommendations of the Royal Commission, of which I had the honour to be a member, will form the basis of a measure to be brought forward in Parliament next session.

But meanwhile what is to be done? Surely we must continue to urge upon the Government that more substantial aid be granted than hitherto has been the case to places where the highest scientific instruction is given, and amongst these the college in the halls of which we are assembled is one of the most deserving.

What, then, we really need at present is a recognition by the State of the necessity of this highest form of scientific education. It is quite true that a large sum of money, about £740,000 a year, is now devoted to what is called "technical instruction," but the greater part of this money is now spent—some may think rightly, though others be of an opposite opinion—in the furtherance of less advanced instruction than is needed for striking out new paths in science. That our craftsmen should be brought up to the level of the requirements of the day is right and proper, and therefore I for one have always upheld the establishing of technical schools throughout the country, even if they did not attempt to do everything. But this technical education of the masses being thus cared for, the equally—or perhaps the more--important national duty of seeing that proper provision is made for those who are to be the future leaders of industry must be attended to.

Whether this can be best accomplished at the older universities, or whether we are rather to look to the younger seats of learning and of research now scattered over the country is an open question. All I desire to intone now is that our legislators and statesmen, as well as the public at large, should be made aware of our national deficiencies, and take to heart the necessity—if England is to retain her supremacy in trade and industry —of making due provision, somehow and somewhere, for that highest training in science which ensures discovery and progress, and upon the application of which all our industries depend.

## THE DURATION OF X-RADIATION AT EACH SPARK.*

### By FRED. T. TROUTON.

THE object aimed at in this investigation was to ascertain how long a Crookes tube continued at each spark to give out Röntgen radiation.

The method adopted was to rotate a metallic toothed wheel—cut out of zinc sheet—interposed between a tube of the "focus" pattern and a sensitive photographic plate protected from ordinary light actions. Only one spark is allowed to pass by making one brake of the primary.

The departure from sharpness of outline of the image of the moving teeth on develpment is observed, and measured in terms of the width of a tooth. If the speed of rotation is known, the length of time the effective radiations persists for can be at once deduced.

A mercury brake worked by hand was generally used. The tube was distant from the plate by about 8 centimetres. When the wheel is rotated sufficiently fast a drawing out of the image is always noticeable, but the amount of its drawing out in each case is found to vary in an important way with circumstances, and is probably but a measure of the length of time the E.M.F. remains above the value necessary for discharge, and thus depends ultimately on the arrangement used—the coil, &c.

If a spark gap in parallel with the tube be provided, the drawing out is cut short on the presence of a spark. How early this occurs depends on the distance apart of the sparking points. In this way comparatively sharp-looking images are obtainable at high speeds of rotation of the toothed wheel, without otherwise altering the arrangements.

* Read before the British Association (Section A), Liverpool Meeting, 1896.

The length the radiation lasted for, measured from photographs obtained in this way, varied continuously from about 1-800th of a second, when no parallel spark is allowed to occur, to 1-10,000th of a second, obtained with the sparking points the nearest possible consistent with getting any effect at all.

These experiments can also be made using a phosphorescent screen. The measurements are not capable of being made with the same certainty, but it is a more convenient way to observe the action of the early cut-off by a parallel spark on advancing or retreating the spark points.

## CONSTITUTION OF THE CARBOHYDRATES OF CEREAL STRAWS.
### FURTHER REPORT OF INVESTIGATIONS.*

By C. F. CROSS and CLAUD SMITH.

IN the Report already furnished to the Committee we have called attention to the results contained in our paper in the *Journ. Chem. Soc.*, 1896. This work, as explained, occupied us from September of last year to the date of publication.

It was also stated that, having elucidated in general terms the constitution of the furfuroids of the *Cereal Celluloses*, and also devised a simple method of separating these constituents, we were about to apply the results and methods to the growing crops (barley) of 1896.

We now have to report that these observations are concluded, and have furnished positive results.

It was shown that the furfuroids of the celluloses from the mature straws had the following characteristics:—

1. The empirical composition of the celluloses, $C_{10}H_{10}O_5$.
2. Yield with phenylhydrazin, however, the osazones *not* of hexoses, but of pentoses (xylose).
3. Yield with hydrogen peroxide, on warming, a characteristic decomposition with formation of a large quantity of $CO_2$.

These results are generalised in a formula showing a pentose and formaldehyd residue in combination, thus:—

$$C_5H_8O_3 \left\langle {}_O^O \right\rangle CH_2.$$
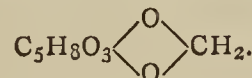
4. The compound, as isolated by acid hydrolysis, is partially fermented by yeast in neutral solution; the solution after fermentation shows a disappearance of about 50 per cent of the furfuroid.

Applying these methods to the diagnosis of the furfuroid *of the growing plant*, we have established the following points:—

1. The furfuroids are separated by hydrolysis with 1 per cent $H_2SO_4$ at 3 atm. steam pressure.
2. *Osazones.* — In the early stages the osazones obtained from the products of such hydrolysis show *high melting-points*—180° to 190°. They are *not*, therefore, pentosazones (which melt at 145° to 155°), but probably hexosazones.
3. *Fermentation* (Yeast).—Up to the flowering period the plant yields, to acid hydrolysis, furfuroids which are *readily and entirely* broken down by yeast.
4. *Hydrogen Peroxide reaction.*—The furfuroids, up to the flowering stage, yield *no carbonic acid* on treating with the reagent at 80° to 95°.

These results differentiate positively the furfuroids of the young growth from the *pentoses*, and also from the *formal-pentoses* of the mature stem.

*In growth, from the flowering period onwards*, we are

* Read before the British Association (Section B), Liverpool Meeting, 1896.

able to diagnose a progressive attainment of the constituent features which belong to a *pentose-formal.*

*Osazones.*—The melting-points are progressively less : those isolated from products from plants cut on July 14th have a melting-point 176° to 178°; on August 14th the osagones had the m. p. 125° to 127°

*Fermentation.*—The furfuroids of July 14th were fermented to the extent of 80 per cent; August 4th 70 per cent; August 14th 55 per cent.

$H_2O_2$ *Reaction.*—The first appearance of the characteristic decomposition, with evolution of $CO_2$, was noticed in the furfuroids from plants cut on August 4th, yielding 4·0 per cent $CO_2$; on August 14th the quantity had increased to 5·5 per cent.

It will be remembered that the celluloses from the mature straws give furfuroids yielding 21 per cent $CO_2$.

These results will be published in full in a forthcoming paper to the Chemical Society.

Recorded here in abstract, they are sufficient to show that our investigations have been productive of positive results, and are based upon a method of attack of the problems involved which is capable of useful extension.

We have now to call attention to conclusions of more general import, and to forecast some developments of our views of *assimilation* in plants.

Our observations on the crops of 1894-5 were directed to estimating the following :—

1. Percentage of furfural obtainable (*a*) from entire plant, (*b*) from its permanent tissue. The proportion *a* : *b* measured the percentage of *easily hydrolysable* furfuroids. This proportion is always small.

Incidentally we made observations on proportion of nitrogen, ash constituents, &c.

On re-calculating the results for the 1895 crop to nitrogen-free, ash-free substance, *i.e.*, to the carbohydrates of the plant, we find the percentage of furfural *to vary but little.* There is a maximum at the flowering period, but the range of variation is slight.

It will be remembered that the furfural (the measure of the furfuroids) is also independent of the conditions of soil nutrition, and but slightly influenced by extreme variations in the atmospheric conditions of growth.

Putting these facts together, they point very positively to the conclusion that the *furfuroids* are *direct* or *primary products* of *assimilation.* There is, of course, no reason in the nature of things why this should not be so; but our ideas have become so fixed upon starch, cane-sugar, or generally the normal hexoses, as the exclusive primary products, that there may be some objections raised to this conclusion on the presumption that it is improbable. The evidence we shall deal with in due course and in greater detail in our paper to the Chemical Society.

Another issue is raised by these observations. Resuming our statement that the assimilation of the barley plant results in the formation of normal hexose groups and furfuroids in the constant proportion of 4 : 1 (approximately), how are these distributed during the whole period of growth ? Up to the time of ear-formation there is no great difference in distribution. But the cereals are characterised by the relatively large weight of seed which they produce. Thus in the growth of 1894-5 which we investigated, the following were the recorded yields of grain and straw :—

|  | PLOT I. | | PLOT 6. | |
|---|---|---|---|---|
|  | Permanently unmanured. | | Maximum fertilisation. | |
|  | Grain. | Straw. | Grain. | Straw. |
| 1894. | 947 | 1291 | 2616 | 3774 |
| 1895. | 415 | 606 | 1616 | 1831 |

The grain being almost constantly 40 per cent of the harvested plant, notwithstanding extreme variations of season and fertilisation.

The seed builds up starch as its preponderating constituent, and the furfuroids of the mature grain are correspondingly low.

After flowering, therefore, the furfuroids are chiefly appropriated to the stem tissues. The question, however, arises—Is this distribution, and more generally is the transference of matter to the seed, a direct process, or is it *indirect ?* *i.e.*, Is it not possible that the stem tissues contribute to seed formation by *depletion* at the ripening stage ? always admitting (for the moment) that both processes may be concurrent.

Upon this point we are accumulating evidence, and it appears probable that we may be able to establish this as a feature of the life-history of plants.

We may point out that the cereals are especially marked out for study of this question, by reason of the extremely high proportion of seed which they form, and also from the presence of furfuroids in large proportion, and fulfilling the *rôle* of a " constant " of the plant.

In our future investigations we shall attack this matter in various ways : by more careful observation of the total weight of the plant, and the variation of gross weight of stem and ear during maturation of the seed : next, by removing the flower and preventing seed-formation, noting the effect on the assimilation in the gross, and the relative assimilation of normal hexoses and furfuroids.

It will be evident, from this abstract and brief forecast, that we have taken advantage of the assistance given us by the Association, and that we have ample prospect of doing further useful work. Should the Association be able to continue the grant, we shall impress more help into the work and be able to compass a wider field.

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## CHEMISTS AS LEADERS.

### By PETER T. AUSTEN, Ph.D., F.C.S.

THE historians of human development speak of the Stone Age, the Bronze Age, the Iron Age, and other ages, meaning thereby the successive periods of human activity that have been characterised by the use of these materials. The most fitting term to apply to the period which began between fifty and a hundred years ago, and whose development is yearly more rapid and more wonderful, would be " The Chemical Age."

In the past, while what was called philosophy marked a high mental activity, much of it was a form of thought based almost entirely on abstract speculation, for the study of matter and its changes was almost unknown. Instead of the exact observation of material objects and their behaviour under varying conditions, and the study of the phenomena of Nature, all kinds of imaginative trains of thought were evolved, and speculations, often baseless, were put forward with little idea as to whether they were supported or not by facts. Even when facts were observed, they were often distorted in order to make them accord with the false or visionary philosophy of the day. But when the delicate balance was invented, and the weights of the different kinds of matter could be exactly determined, and their changes followed with precision, the great principle of the indestructibility of matter was established, and the schools of abstract philosophy suffered an overturn. Instead of the observed fact being subservient to the speculation, the observed fact became dominant, and speculative philosophy retained its value only so far as it accorded with and explained, or amplified by inference, the fact.

All this bears directly upon the conditions of modern competitive life. For instance, men, first of all, must obtain food. To obtain it from weaker communities by force or robbery could be successful only for a time, as the producers were either exterminated, or they gave up so unprofitable an industry. The food supply of mankind

depends on the application of a knowledge of the principles involved in plant growth. The basis of this knowledge is chemistry. It was not really until 1840 that it was demonstrated by the great chemist Liebig that plants, like animals, feed. They take certain kinds of nutriment out of the soil, and soon exhaust it. Soon they fail to grow. Liebig showed that if these nutritive substances were put back into the soil, the plants would keep on growing, and that there was no limit to the productiveness of the earth when properly nourished as chemical science indicated. Malthus stated that the population must be restricted, else it would exceed the food supply. Liebig showed that the production of food-stuffs, made possible by the application of chemical science, was so immense that such a danger is not to be feared. Chemical knowledge has rendered it possible to make several blades of grass grow where there was only one. Liebig then investigated live-stock and proved that, though animals eat many kinds of food, the food owed its value to a few definite nutritive elements that are found in greater or less amounts in all foods; and that the animals, though seemingly widely different in physiological nature, were composed essentially of the same substances. Thus the raising of live-stock and the production of dairy products were placed upon a scientific basis. Agriculture began to employ scientific methods and the cost of raising plants and animals was greatly reduced.

It is not always easy to appreciate at first glance the far-reaching effect of a chemical discovery. The introduction of the hot blast in the manufacture of iron increased the production of pig-iron. The invention by Bessemer of the converter method of making steel practically revolutionised the manufacturing industry of the whole world. What cheap steel means to humanity could not be told in a large volume. The invention of the basic process for treating phosphatic iron ores by Thomas and Gilchrist made it possible to produce steel from ores existing in immense quantities, and hitherto entirely worthless. And, strange to say, phosphorus, the " iron master's curse," is now obtained as a phosphatic slag, which is a most valuable fertiliser for the farmer. The chemist turned the bane of England's iron industry into a blessing to England's agriculture. Weldon utilised the waste product in the manufacture of chlorine, so that it could be used over and over again. In turn was reduced the price of bleach, of bleached white cotton, and of white paper. Books were made cheaper. Education was cheapened. The waste tars of the gas manufacture under the skilful hands of a host of chemists are now the basis of an immense industry. They produce brilliant dyes, perfumes, antiseptics, medicaments, and what not. The astonishing development of chemical knowledge has assisted in the evolution of electricity, the commercial future of which is incalculable. The study of life has been taken up, and by the aid of the colossal genius of Pasteur, disease in plants, animals, and men is checked and avoided, thousands of lives are yearly saved, and the tenure of human existence is far stronger than it was half a century ago. Many pages could be written to illustrate how far-reaching and how little short of marvellous have been the modern advances in chemical science and their applications. But they have taken place so quietly, although irresistibly, that the average individual does not appreciate the part they are playing; nor can we estimate the still greater part they are to play. Another striking instance of the results of chemical research is the development on the one side of explosives, and on the other of hard and tough steel. Without the assistance of the chemist war would be monotonous.

The stability of a community lies in its independence. Its independence is based on its productiveness. Manufacturing consists in changing one kind of form of matter into some other kind of form. It is easy to understand, therefore, that chemistry, the science that studies the changes in the identity of matter, underlies the manufac-turing arts. Hence the industrial status of a nation may be fairly estimated by the condition of its chemical knowledge. It is fair to hold that the country that has the best chemists will, in the long run, be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best clothing, the best manufactured materials, the fewest wastes and unutilised forms of matters, the best guns, the strongest explosives, the most resistant armour. Its inhabitants will make the best use of their country's resources; they will be the most healthy, the most free from disease; they will oppose the least resistance to favourable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition to-day between nations is essentially a competition in the science and applications of chemistry.

It is fair to assume, also, that if men who have devoted their lives to the study and practice of chemical science, and who hence must have the clearest understanding of all men of the true relations existing both between material things and between material things and humanity, also possess the mental calibre that may enable them to be men of affairs, they ought to be especially successful in executive positions. Such an assumption is supported by the fact that the number of responsible positions, at first sight quite unconnected with chemistry, which at present are filled by chemists, or men who have received a chemical training, is large. This shows, not that the chemist is an unusual kind of man, but that a chemical education may make a man unusually efficient. Perhaps as striking an illustration of this as any is the increasing number of chemists in charge of large educational institutions. There is no position in which a man may more powerfully and so lastingly influence man than that of the head of a large school or college.

The Marquis of Salisbury, Prime Minister of England, is a chemist, and spends much of his spare time, when he has any, in his finely-appointed laboratory. And France now places in the most intricate and difficult of positions, that of Minister of Foreign affairs, her most eminent chemist, Berthelot.

These are signs of the time; indications of the chemical age that the world has now entered into, and in which it is destined to remain for many years to come. It will be interesting to watch the course of the two great nations which are now under the guidance of chemists—bearing in mind that Germany is now the home of chemistry, nor forgetting that Russia's advance in chemistry during the last quarter of a century may fairly be called phenomenal.

In this connection it may be pertinent to ask what has become of all the clever and earnest young Japanese chemists who have been studying at the leading educational centres of Europe and America during the last years.—*North American Review.*

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## ON ARGON AND HELIUM.

By SIEGFRIED FRIEDLÄNDER.

The author concludes from his experiments and observations that—

1. Argon which was found incapable of reaction in the numerous attempts of its discoverers, of Berthelot, and of H. Moissan, reacts with platinum, as Troost and Ouvrard had already shown for magnesium on the prolonged action of electrical discharges.

2. Helium is present in the atmosphere at Berlin, as it has also been previously shown at Bonn by Kayser. The quantity is extremely minute. If we consider that the total contents of the tube have to be absorbed, and that in spite of the enormous sensitiveness of spectral analysis the line was observed only with an extremely trifling

intensity, it will not seem exaggerated if we estimate the proportion of helium in the atmosphere as about about 1 : 1000 millions.

3. Helium reacts with platinum on the prolonged action of electric discharges. This has been already observed for magnesium by L. Troost and L. Ouvrard. With aluminium, Bohuslav Brauner has inferred an absorption of helium.

That in the present case only the yellow line was observed is easily explained by the considerable difference in the intensities of the chief lines of helium.

It is remarkable that numerous argon lines lie very near to helium lines without being identical. This similarity in the spectra of the two gases leads us necessarily to the conclusion that the gases themselves must be similar in their behaviour. Now C. Lunge and F. Paschen have shown that helium is not an element, but a mixture of two substances, whence, from a parity of reasons, the inference seems justified that argon is not an element, but a mixture of probably two elements.

For this view the two following facts seem to speak. According to the researches of Lord Rayleigh and Prof. Ramsay the relation of the specific heats is found according to the well-known formula—

$$n\lambda = v = \sqrt{\left[ \frac{e}{d} (1 + at) \frac{Cp}{Co} \right]} \text{ as } 1\cdot61 \text{ and } 1\cdot65.$$

Hence argon would be a monatomic element, and would have the atomic weight 40. But as an element with this atomic weight has no place in the periodic system, the monatomicity of argon has been called in question by several investigators. Thus, *e.g.*, R. Nasini came to the conclusion that we must either reject the results of the kinetic theory of gases or overturn the periodic system. Or, if we assume argon as a diatomic element with an atomic weight equal to its vapour density, with this atomic weight we should uphold the accuracy of the periodic system, but should sin against the kinetic theory of gases, whose conclusions have hitherto shown themselves worthy of recognition. The only remaining assumption is that argon may possibly be not an element —an assumption which has been already convicted by its discoverers.

Crookes has hitherto pointed to the possibility of the compound nature of argon, in reliance upon spectroscopic investigation. J. M. Eder and E. Valenta consider this view as not excluded. But whilst the last-mentioned investigators have examined only the red spectrum of argon, Crookes has observed both spectra, of which the red one is best visible at the pressure of 3 m.m. and at a reduced pressure changes into the blue. Crookes has shown that it is not easy to obtain the blue spectrum quite free from the red, whilst in some circumstances the red spectrum does not change into the blue. Armstrong, indeed, thought this need not be recognised as an evidence of the composite character of argon, since also nitrogen, hydrogen, and oxygen display such spectra. But as hitherto in these elements both spectra have never been seen simultaneously, Armstrong's view need not be accepted as a strict proof of the elementary nature of argon. I myself regard the phenomenon observed, that both the spectra of argon appear simultaneously, as one of the weightiest proofs that Lord Rayleigh and Prof. W. Ramsay have revealed two new elements by their discovery of argon.—*Zeitschrift fur Physikalische Chemie*, vol. xix., p. 657.

**The Cattle Plague in Africa.**—Dr. Edington calculates that £1,000,000 will have to be expended before this scourge is overcome. It was introduced by the Italians, who imported diseased European cattle into their colony at Massowah. It was conveyed up the Nile valley by the Arab caravans, reaching Kilema Njara in 1893. Elephants have been attacked as well as oxen and buffaloes.—*Indian Pharmacologist.*

## SEPARATION OF OZONE FROM HYDROGEN PEROXIDE, AND RECOGNITION OF OZONE IN THE ATMOSPHERE.

By C. ENGLER and W. WILD.

As we have already mentioned in a former communication, chromic acid decomposes energetically hydrogen peroxide, even in the most dilute state, both when the chromic acid is used as a solid, distributed on glass beads, and when applied as a concentrated solution.

We have ascertained by special experiments that chromic acid, either in the solid state or in solution, allows the passage of ozone unchanged. Comparative determinations of the percentage of ozone directly and after passage through chromic acid (effected by titrating the iodine liberated from potassium iodide) gave results perfectly accordant; the discrepancies, distributed quite irregularly, were within the limits of experimental error. If we passed through the chromic acid tube, to which was connected by fusion a T-tube with glass cocks, from the one side a strong current of air which had passed through very concentrated hydrogen peroxide heated to 70°, and carried with it considerable quantities of the latter; and from the other side a slow current of oxygen containing a trifling proportion of ozone, ozone was always easily recognised after the chromic acid. But there was found no trace of hydrogen peroxide, even by means of the most sensitive reaction — the mixture of ferric chloride and potassium ferricyanide. The same result was obtained if we put into a glass flask a little concentrated hydrogen peroxide and some ozoniferous oxygen, and, after previous shaking, sucked it off through a chromic acid tube.

In these experiments we had again opportunity to observe that the mutual decomposition of ozone and hydrogen peroxide in a dilute state ensued very slowly, and that both may be present together for a long time. Nothing could be perceived of an absorption of ozone by the chromic acid modified by hydrogen peroxide.

From these experiments chromic acid appears a suitable agent for deciding the question of the presence of ozone in the atmosphere. This question has been often ventilated, but it has not been decided on account of Schöne's discovery of the presence of hydrogen peroxide in the air. For the decision of this difficult question there are two possibilities. We either employ a reagent which is affected by ozone alone, and not by other constituents occurring in the air, or we first remove those substances which might give the same reaction as ozone; therefore above all hydrogen peroxide. and, in case of certain reagents for ozone, nitrous acid also. The first and simplest method is impeded by the want of suitable reagents, since the reaction hitherto considered as exclusively characteristic of ozone—*i. e.*, the formation of black silver peroxide upon a bright plate of silver—is far from being sufficiently sensitive. However, according to our experiments, paper steeped in a concentrated solution of manganese chloride is suitable for the certain detection of ozone when its change is tested by moistening with tincture of guaiacum.

Ozone turns such paper brown in consequence of the formation of manganese dioxide, whilst hydrogen peroxide—or nitrous acid—has no such effect. The objection was urged by Schöne against the manganese papers that a brown colouration is produced also by means of ammonia and ammonium carbonate. This is quite correct; but the browning produced by the separation of manganese oxide and its oxidation is easily distinguished from that due to ozone. The latter, namely if moistened with solution of guaiacum resin, turns at once blue. The blueness, indeed, appears (as with thallium papers) even before the browning is visible if ozone has been active. But the browning produced by ammonium carbonate yields no such blueness. It scarcely requires mention that the presence of free halogens, hypo

chlorites, &c., must be excluded, since they produce the same reaction,

As for the use of this paper for the determination of ozone in atmospheric air, it seems not sufficiently sensitive, and is in this respect inferior to thallium papers, as they in turn are inferior to potassium iodide starch paper. We prefer, therefore, for the present the second way, and in the first place seek to remove the hydrogen peroxide, by allowing the air to pass first through a tube with chromic acid distributed on glass beads, and then test for ozone on receivers with the different reagents for the ozone. Further experiments must decide whether the traces of ozone which can occur in experiments with atmospheric air pass through when the chromic acid is partially reduced to chromium oxide.—*Berichte.*

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# A GENERAL METHOD FOR OBTAINING THE METALLIC HYDROXIDES ELECTRO-CHEMICALLY.

## By RICHARD LORENZ.

THOUGH it is a very customary reaction to precipitate metallic salts with potassa or soda lye, this procedure is not very well suited for the preparation of the hydroxides. When obtained in this manner they are not readily purified by washing, as they retain obstinately a considerable quantity of alkali-hydroxide. A number of hydroxides are very freely soluble in alkaline lye. These (as *e.g.,* chromium hydroxide, zinc hydroxide, &c.) are consequently not easily obtained in this manner.

These defects may be easily evaded.

In order to obtain certain hydroxides electrochemically there has been hitherto proposed the electrolysis of saline solutions, the chlorides being indicated as the most suitable. If we, *e.g.*, electrolyse a solution of magnesium chloride between platinum electrodes, hydrogen is separated out and magnesium hydroxide is liberated at the kathode. This method seems to have no prospect as a preparative process. It must be pointed out that in salts with anions which do not escape, such as sulphates or nitrates, the use of diaphragms is necessary. Nevertheless the yield of hydroxide is defective on account of diffusion.

Even in the case of chlorides the anion occasioned difficulties. The anodic chloride dissolves in the electrolytes and occasions disturbing by-reactions. Chlorine and metallic hydroxides form hypochlorites. The electrolytic process of bleaching depends on the technical utilisation of this secondary process. Hermite, *e.g.*, submits to electrolysis a mixture of a solution of magnesium alkali-chloride with magnesia, or a mixture of magnesium and calcium chlorides and magnesium hydroxide, and obtains thus his well-known bleaching liquid. These conditions reappear on the electrolysis of chlorides in the laboratory. If, *e.g.*, an excess of magnesium hydroxide is liberated, magnesium hypochloride may readily be formed at the anode.

A third defect of the procedure is the formation of hydroxides at the kathode. The consequence is that the kathodes are generally coated with a non-conductive layer, which may even lead to an interruption of the current. In technical preparation knives are even fixed at the kathodes, which scrape off the incrustations formed.

Finally, this method is very limited. It can serve only for the production of the hydroxides of such metals whose tension of decomposition is greater than that of water. It relates almost exclusively to the production of the hydroxides of the alkaline earths. But if we electrolyse, *e.g.*, solutions of copper or of nickel, the metal separates as such on the kathode, hydroxides not being found at all.

In fine we have, therefore, for the production of metallic hydroxides, a chemical method (precipitation with an alkaline hydroxide) which is general but defective, and an electro-chemical, which is neither general nor useful.

A perfectly universal electro-chemical method, which yields good results, is the following:—We select, according to the conditions of the case, a bath of potassium or sodium chloride, sulphate, or nitrate, and immerse in it a kathode of platinum and an anode of the metal whose hydroxide we seek to obtain. The anion travels to the anode and dissolves it. If we apply, *e.g.*, an anode of cadmium in potassium chloride, there are formed cadmium ions at the anode. Around the kathode there are formed hydroxyl ions by the secondary process. If we agitate the liquid, cadmium hydroxide is deposited in an insoluble precipitate. Even if we were not to agitate, cadmium hydroxide would be gradually formed. The cadmium ion would travel towards the kathode, and on the encounter the hydroxyl ions travelling towards the anode would be precipitated along with them.

This method presents the following advantages :—

1. All the hydroxides insoluble in water may thus be obtained, whether they are soluble in an excess of alkali or not (chemical method), or whether the metals decompose water or not (former electro-chemical method). There are formed hydroxyl-ions and metal-ions in equivalent quantities; thus the hydroxide sought for appears as a precipitate in the neutral solution of an alkaline salt.

2. The precipitate of metallic hydroxide is formed neither at the anode nor at the kathode, but in the solution, like the precipitate from a chemical reaction, but without the reagent.

The consequence is that no coatings are formed at the kathode, the current is not interrupted, and large quantities of precipitate can be separated with the same conditions of current and the same concentrations of the electrolytes.

3. Because the precipitates are formed without the use of a reagent nothing can adhere to them, and they must therefore be distinguished by great purity, supposing the anodes to consist of pure metal. Only the electrolyte used can adhere to them, but an alkaline salt is much more readily washed out by hydroxides than is an alkaline hydroxide.

4. The yield of all hydroxides is very complete, and is almost uniform. The only limit is the solubility in water.—*Zeitschrift fur Anorganische Chemie*, xii., p. 436.

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## ON THE
# COLOUR OF THE ALCOHOLS COMPARED WITH THAT OF WATER.

### By W. SPRING.

OUR knowledge on the relations between the chemical structure of a substance and its colour leaves still much to be desired.

We can indeed establish that certain atomic groups, called on that account chromogens, communicate a more or less intense colour to organic bodies ; but we must admit that we know very little or nothing concerning the colourations displayed by the members of the simplest organic homologous series.

This gap in our knowledge is doubtless founded in the opinion that most organic bodies are colourless. They appear so, in fact, if they are viewed in strata of such thickness as occur in ordinary operations ; but this is no evidence that colouration does not appear if we examine the substances in strata of such depth as to make the absorption of the light directly perceptible. A research conducted on this point of view has the same scientific interest as the determination of any other physical attri-

bute of compound belonging to one and the same homologous series. Such an investigation will doubtless lead to conclusions of value for the explanation of the general properties of matter.

These considerations led me to examine the question whether the monovalent alcohols of the formula—

$$C_nH_{2n},OH$$
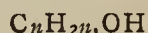
are coloured or not. This class of bodies has been chiefly selected because their chemical properties already known show them to be higher homologues of water, and because the last substance appears colourless only in thin layers. Like water, the alcohols contain in their molecule a constant group, hydroxyl – OH; they are distinguished from water by the fact that they contain a hydrocarbon radicle increasing continually from one compound to the next. This is clearly shown by the following formula :—

HOH.　　　Water.
$CH_3OH.$　Methanol.
$C_2H_5OH.$　Ethanol.
$C_3H_7OH.$　Propanol, &c.

Another reason which decided me to choose this class of substances lies in the possibility that its members, $CH_3OH$, $C_2H_5OH$, and $C_5H_{11}OH$, can be cheaply produced in large quantity and of unquestionable purity.

*The Experiments.*

For observing the colour of the alcohols I made use of the two tubes, 26 metres in length (*Bull. de l'Acad. Roy. de Belg.*, 1896, iii., 31, 95—110), the construction of which is described in my paper "On the Part played by the Currents of the Convection of Heat in the Illumination of Clear Water." One of the two tubes was kept always full of pure water for comparison. The other tube received the various alcohols successively. Neither of the three alcohols examined is colourless in a stratum of 26 metres. Methylic alcohol had a blue colour, slightly inclining to green, as also ethyl alcohol, but with a colder tone. Amylic alcohol is of a greenish yellow. The totally pure blue colour of water changes therefore regularly, becoming more and more mixed with yellow as we ascend in the homologous series.

In the spectrum of water the red is little pronounced, the yellow is expelled, the green very bright, the blue complete, whilst the violet is only transmitted partially. The same property is observed in the spectrum of the alcohols, but the absorption in the violet increases more and more the more the carbon chain predominates, whilst the decrease in the red is little perceptible. The hydroxyl group – OH effects the absorption of the extreme red in the spectrum, and the carbon chains extinguish the opposite end (violet and blue) in dependence on the number of the carbon atom.

Water, H.OH, containing no carbon transmits much violet, methyl alcohol less, and amyl alcohol shows the first blue visible in the spectroscope; nothing is to be seen in the violet. Red remains equally visible in the four substances. The spectrum of ligroin consisted of only three colours—green, orange, and a little red. We may even maintain that the alcohols possessing more than 5 atoms of carbon will include among themselves compounds which entirely extinguish the blue of the solar rays.

The few observations which form the subject of this communication raise several questions the solution of which will not be without interest. Is the tone of the blue colour of an alcohol related to the number of hydroxyl groups of the molecule, i. e., are the polyvalent alcohols more blue than the monatomic? What is the *rôle* of the aldehydic or ketonic hydrogen in colouration? What is the influence of the substitution of the hydrogen of a hydrocarbon of any atoms or groups?—*Zeitschrift fur Anorganische Chemie*, vol. xii., p. 258.

## THE REMOVAL OF SILVER AND GOLD FROM SEA-WATER BY MUNTZ METAL SHEATHING.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry in the University of Sydney.

AMONGST the writers upon the occurrence of *silver* in sea-water, we have Malaguti, Durocher, and Sarzeaud in 1850, Fred. Field in 1856, and Forchhammer in 1865, and as it is difficult for many, especially in this part of the world, to obtain or see the originals, I quote the following extracts from their papers. None of them make any mention of the presence of gold in sea-water or of its removal.

The following extract is from a paper by Messrs. Malaguti, Durocher, et Sarzeaud, entitled—" Recherches sur la présence du plomb, du cuivre et de l'argent dans l'eau de la mer et sur l'existence de ce dernier métal dans les plantes et les êtres organiques " (*Journ. Chem. Soc.*, iii., 1851, p. 69, extracted from *Ann. Ch. Phys.*, [3], xxviii., 129) :—

"*Eetimation of Silver in Sea-water.*—A considerable quantity of sea-water was taken from off the coast of St. Malo, a few leagues from land, and preserved during the course of the experiments in a wooden cistern, from which it was taken out as occasion required in glass vessels. The presence of silver in this water was first demonstrated by the sulphuretted hydrogen process above described; but in order to obtain a more exact estimation of the quantity 50 litres of the water were evaporated to dryness, and the crude salt thence obtained, weighing 1300 grms., was divided into thirteen equal portions, and each portion fused with 30 grms. of pure litharge and 1·13 grm. of lamp-black. This mixture, which was made very intimate by long trituration in a porcelain mortar, was gradually heated to dull redness in a crucible, and maintained at that temperature for fifteen or twenty minutes; the heat was then gradually raised till the mixture fused, and afterwards increased to whiteness; as soon as that temperature was attained, the crucible was withdrawn from the fire. Thirteen operations of this kind yielded 124 grms. of lead, and the silver contained in this was found by cupellation (deducting that which was yielded by the lead alone in a test experiment) to amount to 0·0005 grm. Now, as this demi-milligrm. of silver was extracted from 50 litres of sea-water, it follows that 100 litres —or, for simplicity, say 100 kilogrms. of sea-water—contain 1 m.grm. ; hence the proportion of salt in sea-water is, approximately, one part in 100,000,000, so that a cubic myriametre of sea-water contains 1000 kilogrms., or a cubic mile (English) contains about 2¾ lbs.[†] avoirdupois. This estimation must be regarded as a minimum; for all the preceding operations are attended with slight loss."

In the same paper they refer to the presence of silver in certain fuci, amounting to 1/100,000 ; in various trees such as oak, birch, beech, and apple, also in the blood of an ox and the vegetables upon which it has been fed. They also found it in rock salt and in coal, but as the coal contained pyrites, they do not attach the same importance to its presence in this case.

" On the Existence of Silver in Sea-water," by Frederick Field, F.C.S. (*Proc. Royal Society*, London, vol. viii., 1856-7, p. 292). He examined the sheathings of certain traders as follows :—

"*Ana Guimaraens*, a Chilian vessel, trading up and down the South Pacific for seven years. Yellow metal from the bottom of vessel ; 5000 grains were dissolved in

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* Read before the Royal Society of N. S. Wales.

† The amount obtained by Malaguti, viz., 0·0005 grm. of silver from 50 litres of sea-water, represents over 40 tons of silver per cubic mile, not 2¾ lbs. only, as given in the above translation. Malaguti is not responsible for this error, as it does not occur in the original, where, however, there is also a great error, since 0·0005 g. for 50 litres is said to be equal to 1000 kilos. of silver per cubic myriametre instead of to 10,000,000 kilos.

pure nitric acid and the solution diluted; a few drops of hydrochloric acid were added and the precipitate allowed to stand for three days. A large quantity of white insoluble matter had collected by that time at the bottom of the beaker. This was filtered off, dried, and fused with 100 grs. pure litharge, and suitable proportions of bitartrate of potash and carbonate of soda, the ashes of the filter also being added. The resulting button of lead was subsequently cupelled and yielded 2·01 grs. silver, or 1 lb. 1 oz. 2 dwts. 15 grs. troy per ton. A piece of new yellow metal with which the vessel was being repaired yielded only 0 oz. 18 dwts. to the ton.

*Nina*, a brig just arrived in the Pacific from England. The experiments were performed as before with results :—1700 grs. of the new metal kept in the cabin for possible repairs gave 0·051 gr. = 0·003 per cent = 19 dwts. 14 grs. per ton ; 1700 grs. from the hull, where it had been three years, gave 0·400 gr. = 0·023 per cent = 7 ozs. 13 dwts. 1 gr. per ton.

The amount of silver in the new metal for the *Nina* and *Ana Guimaraens* are unusually low, both being under 1 oz. per ton.

*Bergman.*—A piece from the hull gave 5 ozs. 16 dwts. 18 grs. per ton ; a piece from the cabin gave 4 ozs. 6 dwts. 12 grs. per ton.

*Parga.*—200 grs. from a piece from the hull gave 0·072 grain, and a piece of fresh metal 0·050.

*Grasmere*, only coppered a few months,—610 grains from hull gave 0·075 and from the cabin 0·072 grain.

Mr. Field remarks :—"It will be observed that the amount of silver in the above specimens of fresh metal is very high, and it is probable that most of these are merely the re-rolling of masses of metal melted down from old sheathing, and have derived the greater part of their silver from the sea on former occasions. It is well known that the copper used in the manufacture of yellow metal is very pure, containing 2 or 3 dwts. of silver per ton, frequently not so much, and silver is very seldom associated with the other constituent, zinc. In order to arrive at more certain results, however, I have granulated some very pure copper, reserving some in a glass stoppered bottle, and suspended the remainder (about 10 ozs.) in a wooden box perforated on all sides, a few feet under the surface of the Pacific Ocean, When occasion offers, the box is towed by a line at the stern of a vessel which is trading up and down the coast of Chili. It is almost too soon to expect any decisive results at present, but in a few months I hope to be enabled to send both the original copper and that which has been exposed to the action of the sea."

I do not know whether Mr. Field ever published the results, but I have not come across any reference to them.

"On the Composition of Sea-water in different parts of the Ocean," by Professor Georg Forchhammer (*Phil. Trans.*, 1865, pp. 211, 212):—

"*Silver.*—Malaguti first showed that silver occurs in the organisms of the sea; I have subsequently proved it to exist in a coral, a *Pocillopora*, and several chemists have since tried to prove that silver is precipitated by the galvanic current between the copper coating of a vessel and sea-water. If the last determination is confirmed, the existence of silver in sea-water is proved by direct experiment. From the *Pocillopora alcicornis* I have separated it in the following manner :—I dissolved the coral in muriatic acid, precipitated the solution by hydrosulphate of ammonia, and dissolved the precipitate, which consisted of sulphurets, of phosphate of lime, and fluoride of calcium, in very weak cold muriatic acid, which left the sulphurets of silver, lead, and copper probably mixed with those of cobalt and nickel. These sulphurets were separated from the solution, evaporated to dryness with a little nitric acid, to which were added a few drops of muriatic acid, and dissolved in water, which leaves sulphate of lead and chloride of silver undissolved. When the filter which contained the latter substances is burnt, the silver is reduced to metal; a solution of pure soda will dissolve the sulphate of lead and leave the silver, which, when dissolved in nitric acid, can be tested with muriatic acid. I obtained from *Pocillopora alcicornis* about 1-3,000,000, or from a solid cubic foot of the coral about half a grain of silver."

### Old Muntz Metal Sheathings.

Mr. Cecil W. Darley, late Engineer-in-Chief for Harbours and Rivers, was kind enough to obtain for me some pieces of old Muntz metal sheathing from the piles of wharfs undergoing repair. These were examined for gold and silver with the results given below.

The method used for assaying was as follows :—In each case 2000 grains, except where otherwise stated, of the sheathing in strips were dissolved in 1500 c.c. of pure nitric acid (1 to 3 aq.), free from chlorine. After being cut into strips, the sheathings were boiled in water, beaten, and scrubbed with a brass scratch-brush, so as to get rid of the dirt and scale as far as possible : this probably also had the effect of removing part of the portion richest in gold and silver, as the assays of the separated scale show that it contains more of the precious metals than the body of the sheathing. In most cases the residue was grey and contained much lead. The clear nitric acid solution was decanted and filtered off, and some sodium chloride solution added to ensure the precipitation of all the silver; in the few cases where there was an additional precipitate of silver chloride, this was added to the gold and other insoluble matter on the filter. The solutions varied from green to blue. The filter and residue were dried, wrapped in special assay lead free from gold, scorified, cupelled, and checked in the usual way. In certain cases the sheathing was dissolved in sulphuric acid (but, as the solution took place more rapidly in nitric acid, the latter was preferred), when a yellow substance was generally found on the clock glasses used for covering the beakers; this was found to consist of sulphur containing a little copper, the latter carried up mechanically by spirting; the sulphur was doubtless derived from the sulphuric acid by part of the acid being reduced by the nascent hydrogen given off from the zinc of the alloy, or more probably by the reaction between the hydrogen sulphide and sulphur dioxide evolved.

Sheathing from an old trader, purchased in Sydney about 1874. The solution was made in sulphuric acid as already mentioned.

Silver, 4 ozs. 15 dwts. 9·2 grs. Gold, 1 dwt. 2·4 grs. per ton.

This sheathing was rererred to in a paper on the "Origin of Gold Nuggets (*Journ. Roy. Soc. N.S. Wales*, 1893, p. 331), and was remarkable for containing a good deal of iodine; but none of the other sheathings, since examined, have yielded any iodine.

(*a*) From pile in Mr. Thomas Nobbs's wharf at Ballina, N. S. Wales, between high and low water mark. Exposed four years to sea-water. Corroded, but not so deeply as (*d*).

2000 grains gave—Silver, 6 ozs. 9 dwts. 8 grs.; Gold, 11·8 grs. per ton. Metallic copper, 64 per cent.

(*b*) From longitudinal brace in Ballina Government wharf, N. S. Wales, between high and low water mark. Exposed six years to sea-water.

2000 grains gave—Silver, 2 ozs. 2 dwts. 22 grs.; Gold, 4·7 grs. per ton. Metallic copper, 64 per cent.

(*c*) From piles in Government wharf, Ballina, N. S. Wales, between high and low water mark. Exposed six years to sea-water. Not much corroded and fairly thick metal.

2000 grains gave—Silver, 3 ozs. 19 dwts. 5 grs.; Gold, 19·6 grs. per ton.

2158 grains gave—Silver, 4 ozs. 5 dwts. 14 grs.; Gold, 1 dwt. 7 grs. per ton.

2394 grains gave—Silver, 4 ozs. 12 dwts. 0 gr. ; Gold, 1 dwt. 22 grs. per ton. Metallic copper, 60·3 per cent.

In the last the solution was made with sulphuric acid.

(d) From the pile of Mr. Fenwick's wharf, Ballina, N. S. Wales, wholly submerged for thirteen years in seawater.

So brittle as to break readily between the fingers, with a copper-coloured granular fracture ; hence in parts most of the zinc has apparently been dissolved out. The sheet is much corroded, and very thin on the edge, stained green and brown.

Heated in a tube it emits a "sea-shore" odour, and gives off water which has an acid reaction ; it also yields a fusible sublimate of tarry matter mixed with sulphur. Dissolves entirely in nitric acid, one to three water. The metal when boiled with water yields a solution containing chlorine and a trace of sulphuric acid from sulphates. After boiling with pure dilute sulphuric acid, the metal acquires a copper-red colour and shows a granular or crystalline structure ; a black residue is left, and the solution, on cooling, deposits crystals of lead chloride.

2000 grains gave—Silver, 3 ozs. 14 dwts. 21 grs. ; Gold, 9 grs. per ton. Metallic copper, 62·2 per cent.

*The scale*, first treated with nitric acid :—

227 grains gave—Silver, 1 oz. 10 dwts. 4·4 grs. ; Gold, 15 dwts. 19·5 grs. per ton.

(e) From Irvington, N. S. Wales. Exposed to fresh water ; very little corroded.

2000 grains gave—Silver, 5 ozs. 6 dwts. 8 grs. ; Gold, 19·6 grs. per ton. Metallic copper, 62·3 per cent.

*The scale*, extracted with nitric acid, and the residue scorified and cupelled :—

70 grains gave—Silver, 1 oz., 7 dwts. 23·10 grs. ; Gold, 9 dwts. 8·22 grs. per ton.

(f) From Coraki, N. S. Wales. Exposed to brackish water.

2000 grains gave—Silver, 5 ozs. 6 dwts. 12 grs. ; Gold, 13 grs. per ton. Metallic copper, 63·5 per cent.

(To be continued).

## BACTERIAL ACTION OF POTASSIUM PERMANGANATE, CHROMIC ACID, AND IODINE.

### By ROBERT MELDRUM, F.C.S.

THE following experiments were made with Loch Katrine water to which was added about one-tenth c.c. of urine per gallon and allowed to incubate from 12 to 48 hours. When the water was judged to be sufficiently rich in bacteria, the sample was well agitated and the number of colonies present ascertained. The culture medium employed was that recommended by Frankland, viz., one litre of extract from one pound of lean meat, 100 grms. gelatin, 10 grms. peptone, 5 grms. salt ; the acids present being neutralised with caustic soda. The incubations were conducted for four days at about 75° F. Petrie dishes were adopted instead of plates. For every series of cultivations blank experiments were also made, but with negative results. The temperature during time of contact would be about 60° to 65° F.

Out of a total of 32 experiments it will be noted that complete sterilisation only resulted in two cases. It is remarkable that a strength of 42 grains per gallon of such a powerful oxidiser as potassium permanganate should not produce complete oxidation of such minute organic bodies even in five minutes, whereas a strength of nearly one-sixth of that should produce nearly complete sterilisation, This uncertain action is not uncommon to the salts investigated, and may probably be explained by (1) an excessive quantity of soluble organic matter being present which consumes the greater part of the salt before it has time to exert a destructive action on the organisms ; or by (2) the presence of bacteria in the internal parts of both organised and unorganised particles which are present in the water, and in this way being protected from the action of the reagent for a considerable time ; by (3) the life-history of the organisms. The latter theory is the more likely.

### Bacterial Action of Permanganate.

| Grains Permanganate per gallon. | Colonies of Bacteria per c.c. before treatment. | Colonies of Bacteria per c.c. after treatment. | Time of contact in minutes. | Remarks. |
|---|---|---|---|---|
| 1·4 | Innumerable. | Innumerable. | 5 | Gelatin liquid in 48 hours. |
| 1·4 | ,, | ,, | 5 | |
| 2·8 | ,, | ,, | 5 | |
| 2·8 | 30,000 | 300 | 5 | |
| 2·8 | 1000 | 10 | 10 | |
| 7·0 | Innumerable. | Innumerable. | 5 | Gelatin becomes liquid. |
| 7·0 | ,, | ,, | 5 | |
| 7·0 | ,, | ,, | 5 | Gelatin becomes liquid. Cols. mostly pin head. |
| 7·0 | 30,000 | 200 | 5 | |
| 7·0 | 6000 | 80 | 10 | |
| 7·0 | ,, | 50 | 20 | |
| 7·0 | 1400 | 60 | 30 | |
| 7·0 | ,, | 40 | 40 | Nearly all chromogenic colonies. |
| 7·0 | ,, | 25 | 60 | |
| 7·0 | 2000 | 100 | 5 | |
| 7·0 | ,, | 9 | 10 | |
| 7·0 | Not determined. | 0 | 10 | |
| 7·0 | 1000 | 15 | 10 | Chromogenic colonies. |
| 7·0 | ,, | 4 | 20 | |
| 7·0 | 300 | 4 | 5 | |
| 7·0 | ,, | 3 | 10 | |
| 7·0 | ,, | 3 | 30 | |
| 14 | 30,000 | 100 | 5 | Pin head colonies. |
| 14 | ,, | 120 | 5 | |
| 14 | 1400 | 60 | 10 | Some cols. chromogenic. |
| 14 | ,, | 40 | 20 | |
| 21 | 60,000 | 100 | 5 | Nearly all liquefy gelatin. |
| 21 | ,, | 130 | 5 | Mostly pin head cols. |
| 32 | 1000 | 3 | 10 | All chromogenic. |
| 32 | ,, | 0 | 20 | |
| 33 | 6000 | 200 | 5 | Liquefies gelatin. |
| 42 | ,, | 200 | 5 | |

### Bacterial Action of Chromic Acid.

| Grains of Chromic Acid in gallon. | Colonies of Bacteria per c.c. before treatment. | Colonies of Bacteria per c.c. after treatment. | Time of contact in minutes. | Remarks. |
|---|---|---|---|---|
| 7 | About 30,000 | 2000 | 10 | Nearly all pin head colonies. |
| 14 | ,, | 3000 | 10 | |
| 28 | About 2000 | 100 | 10 | |
| 28 | ,, | 10 | 10 | |

### Bacterial Action of Iodine.

| Strength of Solution in grains per gallon. | Colonies of Bacteria in c.c. before treatment. | Colonies of Bacteria in c.c. after treatment. | Time of contact in minutes. | Remarks. |
|---|---|---|---|---|
| 2·8 | Innumerable. | 12 | 5 | Iodine in pot. iodide 1 I to 3 KI. |
| 2·8 | ,, | 3 | 15 | |
| 2·8 | 1000 | 1 | 5 | |

Of the three agents examined iodine seems to be the most powerful.

Laboratory, 196, St. Vincent Street, Glasgow.

Action of Oxygen upon Alcoholic Liquors.—It has been recently established that the "fusel" in raw spirits can be removed by the introduction of a current of pure oxygen. The flavour of the spirit is not only improved, but its physiological action is much ameliorated.

# NOTICES OF BOOKS.

*A Tabular Atlas of the Chemistry of the Metals.* Comprising the Arrangement on a Novel Plan in Sectional and Tabular Form, devised to rapidly convey Information on the Data relating to the History, Distribution, Preparation, or Metallurgy Properties; Chemical, Medical, Pharmacal, and Technical Uses; Analysis and Toxicology of the said Metals, their Organic and Inorganic Compounds. *Metals of the Alkalies, Cæsium, Rubidium, and Potassium.* By JOHN FREMONT SLEEPER.

OUR opinion of this work, judging from the specimen which has fallen into our hands, cannot be other than favourable. It is a cyclopædia of the metallic elements and their compounds, both with each other and with the non-metals.

The plan followed is apparently novel as applied to literary matter; it has been actually patented. The exact claims of the patent will be, we think, difficult to define.

The names of the substance will be found in vertical columns at the left-hand of each page, whilst in horizontal columns come in succession the preparation (or occurrence), the colour, crystalline form, &c.; the reaction (presumably with litmus), the specific gravity, the formula, the solubility in water at 15° and at 100°, in absolute alcohol, in sulphuric acid, nitric acid, hydrochloric acid, potassium hydroxide, ammonia, ammonium chloride, alkaline carbonates, acetic acid, ether; behaviour on exposure to air and light, to heat, on fusion with a number of substances, on ignition; the molecular weight, and we presume the atomic weight if an element; the percentage composition; and, lastly, miscellaneous information. The information required is to be sought at the intersection of the vertical and the horizontal column.

As an instance of the extent and accuracy of the information given, we may mention that the instructions for the quantitative analysis of potassium salts occupy some twenty pages.

We cannot help regarding the heading "proprietary preparations" (or, in plain old-fashioned language, quack nostrums) as emphatically below the dignity of such a work as that before us.

The physical and chemical characters of each metal are arranged under the headings—Equivalence; atomic volume; atomic weight; specific heat; specific gravity; colour and crystalline form; hardness; malleability; ductility; electric conductivity; refraction equivalent; permanence in air; permanence in water; on exposure to heat; action of solvents; exposure to the action of the following inorganic substances; ditto, of organic substances.

In the Prospectus we are advised to compare the specimen of the work on potassium compounds with the data given in Watts, Wurtz, and Gmelin, and note "how unsatisfactory in comparison will be the information they impart." An opinion quoted even says that the work "will elevate American scientific authorship above the level of the English and the German."

That Mr. Sleeper's *magnum opus* will be of immense value is indisputable, and we hope that it will be appreciated as it merits.

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*Kemp and Co.'s Prescribers' Pharmacopœia.* A Synopsis of the more recent Remedials, Official and Unofficial, with a Therapeutic Index. Third Edition. Bombay: Kemp and Co., Ltd.

PENDING the avatar of the long-promised Imperial Pharmacopœia, the book before us is likely to prove of great use in India and the tropical colonies. The climatic requirements of such regions, as regards solubilities, &c., have been carefully considered. A contemporary refers to the difficulties of dispensing when the thermometer at the dispensing counter marks 100° F. A very valuable feature is the notice of indigenous Indian drugs which may serve as substitutes for European or American products.

The chief thermometric scales are given, though that of Réaumur is now scarcely necessary. A table of hydrometer scales might have been given, so far at least as to show the comparison of Twaddell's scale with direct specific gravity. For Baumé there is no occasion.

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# CORRESPONDENCE.

## THE SCIENCE AND ART DEPARTMENT.

*To the Editor of the Chemical News.*

SIR,—In one respect, at all events, your correspondent "S." is mistaken with regard to the new regulations of the Science and Art Department; I refer to that of the three stages. I entered for the elementary examination in Practical Chemistry in company with an acquaintance who was up for the Honours; we both passed. The next year I presented myself for the advanced, and he for the elementary stage (as he could not obtain his Honours certificate). This time the examiners were kind to me, but not to him. Consequently, although this happened nearly twenty years ago, my fellow candidate has nothing to show for his Honours to this day.

Possibly "payment on results" is in the first place responsible for this deplorable state of things, but by preventing a repetition of it the Department, so far from being retrograde, has made a step in advance.

That it should have been possible to pass in Honours without any knowledge of the fundamental principles of the science, is not only a disgrace to the Department, but to the nation also!—I am, &c.,

W.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 12, September 21, 1896.

This issue contains no chemical matter.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 3.

Contributions to the Examination of Honey.—Some portions of this voluminous memoir will be inserted in full.

Further Remarks on the Quantitative Separation of the Proteid Substances present in Beer Wort.— H. Schjerning.—This paper, which is a communication from the laboratory of Neu-Carlsberg, is too extensive for insertion.

Double Compounds of Aniline with Metallic Salts. —J. L. C. Schrœder van der Kelk.—The compounds of ferric salts with aniline except ferric chloride have not been prepared, and, like the latter, they are not applicable in microscopic practice. The process is perfectly useless for the detection of iron, but the reactions for cobalt and nickel are available.

Determination of Nicotin and Ammonia in Tobacco.—Dr. Viktor Vedrödi.—A reply to the objections made by Kissling to the author's process (*Zeitschr. Anal. Chem.*, xxxiv., p. 413).

New Volumetric Method of Determining Soluble Compounds of Iodine.—Prof. Dr. E. Riegler.—Already inserted.

Quantitative Determination of Zinc in Organic Salts.—Gottfried van Ritter.—The zincic salt is covered with concentrated nitric acid, the acid is cautiously evaporated off, and the residue is ignited. The zinc is left behind as oxide. The author gives instances of the accuracy of his method as applied to zinc acetate, lactate, succinate, tartrate, mucate, benzoate, and hippurate. The excess of nitric acid must be driven off at a gentle heat, to avoid spirting, and the apparently dry residue must not be at once ignited, but merely heated a little more strongly than before. These two operations can be easily and safely executed in a Lieben muffle. The residue is then heated until white. Porcelain crucibles should be used, as platinum is strongly attacked. Experiments in which sulphuric acid was used instead of nitric acid gave results too high by several per cents.

Behaviour of Nitrogenous Organic Bodies with Potassium Polysulphides at High Temperatures.— Heinrich Aufschläger.—A great number of nitrogenous substances, inorganic as well as organic, was investigated, and the transformation of nitrogen into sulphocyanogen was found to be a universal reaction of nitrogenous bodies. The field of potassium sulphocyanide is about 10 per cent of the quantity theoretically possible.

Occurrence of Iodine in Water.—Prof. Dr. Lecco. — Besides the iodiferous saline springs sea-water is generally considered the only water containing iodine. The statements found in literature concerning the presence of iodine in other waters are often discordant. In researches dating back to 40 years ago and beyond it was stated that almost every water contained iodine, as also the air, the earth, and the majority of animal and vegetable substances. Subsequent authorities have been unable to show the presence of iodine in air, water, &c. This discrepancy may be explained either by assuming that the reagents used were nor always sufficiently pure or that some of the methods used for the detection of iodine are defective. The reaction for iodine with nitrous acid and carbon disulphide is so sensitive that those quantities of iodine which occur, e.g., in iodiferous salt springs, are easily detected. In mineral waters which contain per litre only 0·1 m.grm. iodine it is almost always possible to detect the iodine directly and determine it colorimetrically without previous concentration. The author then gives an account of the Belgrade drinking waters, which are chiefly bad. In the good waters it was fairly easy to recognise iodine, but of the twelve town wells examined which yield bad water traces of iodine—scarcely perceptible—were recognised in one only. Hence the question arises whether the direct recognition of iodine in water does not bear some relation to other constituents of water which possibly interfere with the ready detection of iodine in bad waters. The author's results show that iodine is more generally diffused than is ordinarily assumed. He intends to continue his experiments on the occurrence and the detection of iodine.

# THE CHEMICAL NEWS.

## THE DETERMINATION OF SULPHURIC ACID, OR OF BARIUM.

### (A PRELIMINARY COMMUNICATION).

By JAMES EDMUNDS, M.D., F.C.S,, &c.,
Medical Officer of Health and Public Analyst for St. James's,
London.

I VENTURE to submit a process by which, in about fifteen minutes, we may make an extremely close measurement of the sulphuric acid in a small quantity of any ordinary liquid—say, in 70 c.c. of a sulphatic water.

The process is straightforward and easy, and it requires no heating. The reagents are anhydrous salts, —easily obtained in a state of extreme purity, and, in storage, undergoing no change and attracting no moisture. Their solutions are permanent.

In accuracy of measurement the process equals that of a chlorine or silver titration, if only imperfect manipulation, and errors as to the purity, strength, and measurement of the reagents be excluded.

*Scheme.*—The $SO_3$ to be measured is precipitated with barium nitrate in excess, the residual barium is precipitated with potassium chromate in excess, the residual chromate is precipitated with silver nitrate in excess. The mixture is filtered off. An aliquot part of the filtrate is titrated for its residual silver nitrate, potassium chromate being used as indicator. The total of the residual silver nitrate, deducted from the silver nitrate originally introduced, gives the equivalent of the $SO_3$.

The solutions required are :—

| | | | |
|---|---|---|---|
| 1. | Barium nitrate.. .. .. | N/10 and N/100 | |
| 2. | Potassium chromate .. | N/10 and N/100 | |
| 3. | Silver nitrate .. .. .. | N/10 and N/100 | |
| 4. | Sodium chloride .. .. | N/10 and N/100 | |
| 5. | Potassium thiocyanate .. | N/100 | |
| 6. | Ferric sulphate .. .. | N/10 | |
| 7. | Calcium sulphate .. .. | N/100 | |
| 8. | Potassium sulphate .. | N/10 and N/100 | |

The ferric sulphate is made from a solution of crystals of ferrous sulphate by boiling with nitric acid to full peroxidation of the iron, then adding sulphuric acid in large excess, and boiling off residual nitric acid so as to leave a solution of pure ferric sulphate in pure sulphuric acid. The residue is made up to volume as a N/10 solution of iron in about 5 N sulphuric acid.

This ferric indicator gives no blue colour with freshly-made solution of potassium ferric cyanide; it does not bleach permanganate, and it never evolves nitrous fumes. It keeps perfectly.

The calcium sulphate is made by weighing out 0·860 of pure selenite into a standard flask, and then adding freshly-boiled distilled water to 1000 c.c. at the standard temperature. It serves for experimental work and for control in the titration of sulphatic waters.

The potassium sulphate is used for experimental work and for general control.

*Process.*—Seventy c.c. of the titrate* is measured out into a 200 c.c. tall glass-stoppered bottle. Ten c.c. of N/10 solution of each reagent successively is then added, —the barium first, the chromate next, the silver last,—and the mixture is shaken vigorously for one minute after the

* The term titrate is used to indicate a liquid in course of titration.

addition of each reagent. The mixture is poured into a filter, and a bright colourless neutral filtrate runs rapidly through.

An aliquot part of the filtrate—say 20 c.c.—i s measured out into a white basin, an accurately measured round volume of N/10 sodium chloride is added so as to overdo the residual silver by 0·2 to 0·5 c.c., and the solution is then distinctly yellowed by adding potassium chromate. New silver, as N/100 $AgNO_3$, is now slowly dropped in, with active stirring, until silver chromate begins to redden the titrate permanently.

The chloride used, *minus* the new silver, gives the aliquot portion of the residual silver nitrate. The total residual silver, deducted from the amount of silver originally added, gives the silver shortage. The shortage of the silver is the equivalent of the $SO_3$.

If the final result be not needed at once, the mixture may preferably be set aside till next day. Part of the clear supernatant solution may then be withdrawn for titration, and there is no filtering and no disturbance of volume to correct for.

If extreme precision and immediate results are needed, I filter off the mixture at once (by means of a little apparatus of my own) directly into a standard pipette or burette. In this way transference of the mixture from its tall glass-stoppered bottle is avoided, while disturbance of volume (by reason of evaporation during filtration) is entirely excluded. This little apparatus is quite simple and of great general utility, but the present crowded condition of the columns of the CHEMICAL NEWS compel me to defer its description and diagram.

In titrating attenuated sulphatic solutions, such as the London drinking waters, centinormal reagents may be substituted for the decinormal. Or, such waters may be concentrated by adding successive volumes in a boiling-down flask, and, when cold, making up to volume with freshly-boiled distilled water. After mixing, and subsidence of the $CaCO_3$, an aliquot part of the clear supernatant liquid is withdrawn for titration. In technical work the routine may be modified by instituting a dosage different from the uniform 10 c.c. of each reagent. Of the solution, 70 c.c. is a convenient quantity to handle; its result expressed in m.grms. is grains per standard English gallon; one hundred sevenths of the result is m.grms. per litre. The 100 c.c. of the mixture is a convenient quantity to divide and to calculate for.

Strong sulphatic solutions should be attenuated for titration to about centinormal strength.

It will be seen that each precipitate is thrown out in the presence of an ample excess of its precipitant. This excludes the influence of any neutral zone.

A minute quantity of silver chromate would remain in solution in a filtrate charged with certain salts. Such silver chromate is compensated for exactly by using the potassium chromate indicator in the titration of the residual silver. Mohr's beautiful indicator in this case has its one defect converted into a special excellence.

*The Titrate.*—In some cases the titrate will need preliminary examination and preparation with a view to eliminate or to allow for interferent substances.

1. Phosphoric and other acids which would precipitate barium otherwise than as sulphate, should be eliminated by shaking with milk of pure lime in slight excess, boiling, passing in carbon dioxide, boiling, filtering, and washing the precipitate. This procedure would also eliminate ammonia and magnesia.

2. Lead, sulphur compounds, and other substances which would precipitate or reduce chromic acid must be eliminated.

3. Haloid radicles, and other precipitants of silver, are best measured in a preliminary volume of the solution, and ultimately deducted from the shortage of silver as calculated from the final titration. A preliminary volume of the solution is shaken with a measured volume of N/10 silver nitrate in excess, the precipitate is filtered

off and the filter washed, and the residual silver is then titrated by means of thiocyanate with ferric sulphate.

4. Carbonic acid may be boiled off if necessary. The solution, if not neutral, must be carefully neutralised by means of N/10 soda or acetic acid. Any alterations in volume which supervene in preparing the solution, or in filtering off the titrate, must be redressed or taken into account.

In determining barium, 70 c.c. of its solution is shaken with 10 c.c. of N/10 solution of $K_2SO_4$. The residual $SO_3$ is then determined by the procedure above described. The 70 c.c. must contain less barium than is equivalent to the $SO_3$ in the 10 c.c. of $K_2SO_4$, and it must be free from substances—such as strontium or lead—which would precipitate $SO_3$ otherwise than as $BaSO_4$.

29, Dover Street, Piccadilly,
October 2, 1896.

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## LIMITING THE EXPLOSIVE PROPORTIONS OF ACETYLENE, AND DETECTING AND MEASURING THE GAS IN THE AIR.*

By Professor FRANK CLOWES, D.Sc.,
University College, Nottingham.

THE value of acetylene as an illuminant, and the discovery of its ready production from calcium carbide, have led to the manufacture of this gas in some quantity; and acetylene will probably be dealt with in still larger volume in the near future. It becomes, therefore, important to devise methods of detecting its presence in the air, arising from leakage and escape, and to measure the percentage of the gas present at any place. It is also important to ascertain what proportions of the gas, when present in mixture with air, will lead to explosion if the mixture should be kindled.

The detection of small proportions of the gas will not be readily effected by its smell when it is prepared in a state of purity. At present the smell is made much more pronounced by the impurities which the commercial gas contains. Further, the smell will not in any case furnish a means of measuring the proportion present in the air. The method applied by the writer to the detection and measurement of fire-damp and coal-gas in the air, however, serves for detecting and measuring acetylene as well. A small hydrogen flame, set to either 5 or 10 m.m. in height, as may be necessary, shows a pale but well-defined " cap " in air containing any proportion of acetylene less than the lowest explosive proportion. When the hydrogen flame is exposed to the air to be tested for acetylene in a darkened space, it is at once tinged yellowish-green. The bluish pale cap has the following heights with varying proportions of acetylene, when the hydrogen flame is 10 m.m. in height :—

0·25 per cent gives 17 m.m. cap.
0·50   ,,     ,, 19   ,,   ,,
1·00   ,,     ,, 28   ,,   ,,
2·00   ,,     ,, 48   ,,   ,,

When the hydrogen flame is reduced to 5 m.m. —

2·50 per cent. gives 56 m.m. cap.
2·75   ,,     ,, 79   ,,   ,,

A convenient portable form of apparatus was shown by the writer, which enabled air to be passed readily over the standard hydrogen flame in a darkened vessel, and which quickly furnished the reading of the height of the cap.

In determining the limits of explosibility, when acetylene is mixed in gradually increasing proportion with air and kindled, the writer adopted a simple method, referred to at the last meeting of the Association. It was found

* Abstract of a Paper read before the British Association (Section B), Liverpool Meeting, 1896.

that air must contain at least 3 per cent of acetylene before it can be kindled by a flame and the mixture caused to burn throughout. As the proportion of acetylene is increased, the explosive character is augmented. When 22 per cent of acetylene is present, carbon begins to separate during the burning. The amount of carbon which separates increases until the explosive character of the mixture disappears. This point is reached when 82 per cent of acetylene is present in the air.

The limiting percentages in air which are explosible are accordingly as follows, and may be compared with those already determined by the writer for other combustible gases :—

| | |
|---|---|
| Acetylene   .. .. .. .. | 3 to 82 |
| Hydrogen   .. .. .. .. | 5 ,, 72 |
| Carbon monoxide .. .. .. | 13 ,, 75 |
| Ethylene .. .. .. .. .. | 4 ,, 22 |
| Methane .. .. .. .. .. | 5 ,, 13 |

It will be seen that acetylene gives a wider range of explosive proportions than any other of these gases does. Probably this is due to its endothermic nature, which leads to the gas being able to generate heat by its own decomposition. Heat thus generated would undoubtedly aid in causing explosion, and would thus extend the limits of explosive mixtures.

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## THE DETECTION AND ESTIMATION OF CARBONIC OXIDE IN THE AIR.

By Professor FRANK CLOWES, D.Sc.,
Universtiy College, Nottingham.

CARBONIC oxide gas, when mingled with air in suitable proportion and fired, produces explosion. But a far greater danger arises from its poisonous nature when breathed. As small a proportion as 0·2 per cent in air produces poisonous symptoms on man. This gas is introduced into the air by leakage of unburnt water-gas and other gaseous fuels, amongst which ordinary coal-gas must be included. It is produced in the coal-mine by the firing of certain explosives, such as blasting powder and the nitro-cottons; also during an explosion of fire-damp, or by burning of coal or gob-fire. Hence carbonic oxide may be frequently encountered in air; and since it cannot be smelt or detected by any ordinary tests, it is important to make known recently devised methods for detecting and estimating the gas.

Dr. Haldane has brought forward a method which depends upon the change in colour produced in diluted blood when it is shaken up with the gas. This is probably the most delicate and accurate method known. But it requires some time for its performance, and good daylight is an absolute necessity.

Other methods are well known to the chemist which are not sufficiently delicate, and require to be carried out in a chemical laboratory.

The author recommends the flame-cap test as being at once quick of execution, sufficiently delicate, and also wide in its range of indications. The standard hydrogen-flame, 0·4 inch in height, gives a cap 0·5 inch in height in air containing 0·25 per cent of carbonic oxide, and the height of the cap increases as the percentage of carbonic oxide in the air becomes larger. The only drawback of the method consists in the fact that all combustible gases give flame-caps, and these are indistinguishable from that furnished by carbonic oxide. Hence the flame-cap test is only suitable when other combustible gases are known to be absent.

The test may be made by introducing into the air to be examined a hydrogen safety-lamp, such as has been now adopted in delicate tests for fire-damp and coal-gas. Since, however, there might be serious risk involved in entering and breathing the atmosphere, it is preferable to

collect a sample of the air and pass it over the flame, as is done by Mr. Redwood in testing for petroleum vapour. A still more simple plan will often consist in pumping the air to be tested over the standard hydrogen-flame in a suitable apparatus, such as was exhibited by the writer. It consists of a small metal cylinder with glass front, within which the hydrogen-flame burns, being fed from a pocket cylinder of the compressed gas. The cylinder containing the flame is mounted on a folding portable camera tripod. The air to be tested is drawn through a long rubber-tube, by working a valved rubber ball by the hand, and is made to pass over the hydrogen flame. A black cloth is thrown over the observer's head and the flame-cylinder, so as to enable the flame-cap to be accurately observed in darkness, and the height of the cap is registered by shifting a bent wire, moving stiffly in a stuffing box, until it just touches the tip of the cap. On removing the black cloth, the percentage of carbonic oxide is then at once read off upon a scale on the cylinder, the number standing opposite to the top of the movable wire. Other details of the method will be found in a book on the "Detection and Estimation of Inflammable Gases in the Air," which has been recently published for the writer by Messrs. Crosby Lockwood and Sons.

The flame-cap test applied in this way presents the advantage of being rapid and delicate, and may be applied without any risk to the operator.

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## ESTIMATION OF SULPHUR IN ORES.

### By J. H. STANSBIE.

THE following modification of the usually described process for the estimation of sulphur in ores is found to give accurate results, and to require a much shorter time for its completion :—

About 0·5 grm. of the finely-powdered ore is weighed into a beaker, and 10 c.c. of strong nitric acid added. The acid is then raised to boiling, and the action continued until the sulphur has largely separated out and is floating on the surface of the liquid in globules. The beaker is then removed from the hot plate, and allowed to cool. When cool about 1 c.c. of bromine is added. The globules of sulphur are at once taken up by the bromine. The beaker is then gently warmed for a few minutes on the hot plate, the clock-glass removed, and the liquid evaporated just to dryness. About 5 c.c. of strong hydrochloric acid are added, and the beaker heated until the residue is completely removed from the bottom. About 100 c.c. of hot water are now added, and the contents of the beaker boiled for two or three minutes. The siliceous residue is then filtered off, and the filtrate is ready for the precipitation of the sulphate by barium chloride.

If rapid working is of importance, the whole of the operations described above may be carried out in less than an hour. The solution for the estimation of the metals present may be prepared in a similar manner.

As a check upon the method, it was worked in conjunction with another method which has been found to give good results with several sulphide ores :—

About 0·5 grm. of the finely-powdered ore is weighed in a porcelain crucible, and 3 grms. of pure lime is gradually mixed with it by stirring in a little at a time with a thin glass rod. The crucible is then placed in a moderately hot gas-muffle, and left for an hour.

The contents of the crucible are transferred to a beaker, a little water added, and then a few drops of bromine, to ensure complete oxidation of the sulphur to sulphate. The solution is heated, hydrochloric acid added (a little at a time), and the liquid boiled until all the soluble matter is dissolved. The solution is filtered from the siliceous residue, and the sulphate precipitated

from the filtrate by barium chloride. The following results were obtained :—

#### 1.—*Artificial Cuprous Sulphide.*

By nitric acid and bromine.. .. 20·94 per cent sulphur
By roasting with lime .. .. .. 20·97 „ „

#### 2.—*Copper Pyrites.*

By nitric acid and bromine.. .. 27·46 per cent sulphur
By roasting with lime .. .. .. 27·41 „ „

To prove the completeness of the oxidation of free sulphur by nitric acid and bromine, 0·1126 grm. of pure sulphur was treated with the mixture, the solution neutralised with sodium hydroxide free from sulphate, evaporated to dryness with hydrochloric acid, to get rid of nitric acid and bromine, taken up with a little hydrochloric acid and water, and the sulphate precipitated by barium chloride.

0·8198 grm. $BaSO_4 = 0·11258$ grm. sulphur was obtained.

As far as the writer is aware, the powerful and extremely rapid action of a mixture of nitric acid and bromine upon free sulphur has not been noticed before, and from his experiments he is convinced that it is well worth the attention of those who are frequently dealing with sulphide ores.

Metallurgical Laboratory.
Municipal Technical School, Birmingham.

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## THE DETERMINATION OF TELLURIUM BY PRECIPITATION AS THE IODIDE.*

### By F. A. GOOCH and W. C. MORGAN.

IT was known to Berzelius that hydriodic acid and tellurous acid interact with the formation of tellurium tetraiodide, which is converted by water into an oxyiodide and by excess of an alkaline iodide into a soluble double salt. Wheeler (*Amer. Journ. Sci.*, xlv., 267) has shown that the double salt which is formed when tellurous iodide is boiled in a strong solution of potassium iodide in dilute hydriodic acid is definite, and has the constitution represented by the formula $2KI.TeI_4.2H_2O$. We have observed, however, that when potassium iodide is added to a cold solution of tellurous acid containing at least one-fourth of its volume of strong sulphuric acid, no tendency toward the formation of a double salt becomes apparent until the potassium iodide amounts to more than enough to convert all the tellurous acid present into the tetraiodide according to the equation—

$$H_2TeO_3 + 4H_2SO_4 + 4KI = TeI_4 + 4KHSO_4 + 3H_2O.$$
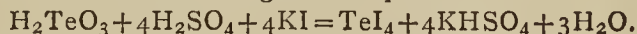
The tellurium tetraiodide which is thus formed is extremely insoluble in sulphuric acid of the strength mentioned, though soluble in excess of potassium iodide, and acted upon by water with the formation of tellurium oxyiodide and hydriodic acid. It is produced at first in the condition of a finely divided dark-brown precipitate, which upon agitation of the liquid containing it gathers in curdy masses and settles, leaving the supernatant liquid clear. By taking advantage of this tendency to curd it is possible to determine without great difficulty the exact point during the gradual addition of potassium iodide when the precipitation of the tellurium iodide is complete, and we have been able to found upon this property a very simple titrimetric method for the direct determination of small amounts of tellurium.

In our test experiments we used tellurium dioxide prepared by oxidising presumably pure tellurium with nitric acid and igniting the residue at a low red heat. Weighed

amounts of the oxide thus prepared were dissolved in Erlenmeyer beakers in a very little of a strong solution of potassium hydroxide, and dilute sulphuric acid was added carefully until the tellurous acid which was precipitated upon the neutralisation of the alkaline hydroxide was just re-dissolved. To this solution sulphuric acid of half-strength was added in such amount that the solution finally obtained, after adding the aqueous solution of potassium iodide subsequently, should still contain at least one-fourth of its volume of strong sulphuric acid. The Erlenmeyer beaker was placed upon a pane of window glass supported upon strips of wood about 1 c.m. above the level of the work table, which was covered with white paper. A solution of approximately decinormal potassium iodide free from iodate, and carefully standardised in terms of iodine by a method described in a former paper from this laboratory (*Amer. Journ. Sci.*, xxxix., 188; xlv., 334), was introduced gradually from a burette into the middle of the Erlenmeyer beaker. As the drops of the potassium iodide touched the liquid the precipitation formed at the centre and travelled in rings toward the outer walls of the beaker. When the liquid became so opaque that the effect of the potassium iodide was distinguished with difficulty, the beaker was rotated and the curded precipitate permitted to settle, and then the process of titration was continued as before. We experimented with amounts of tellurium dioxide varying from approximately 0·025 grm. to 0·1 grm., the latter quantity being as large as can be handled with accuracy without intermediate removal of the precipitate by filtration. With an Erlenmeyer beaker 10 c.m. in diameter across the bottom, and a final volume of liquid amounting to not more than 100 c.m.³, we were able to follow the precipitation most easily.

The results of a series of determinations made according to the method described and recorded in the following table are closely accordant, and in close agreement with the theory of the process if the atomic weight of the tellurium which we used is taken as 127. We feel justified in taking this number as the atomic weight of our tellurium, because the mean result of twelve oxidations by standard potassium permanganate of tellurium dioxide, prepared similarly to that which we used, and from the same lot of material, and the mean result of twelve reductions by hydrobromic acid of the telluric acid thus produced (*Amer. Journ. Sci.*, xlviii., 377 and 378), point to this figure.

| Final volume. C.m.³ | Strongest H₂SO₄ present. C.m.³ | Iodine value of KI used. Grm. | TeO₂ taken. Grm. | TeO₂ found. Grm. | Error. Grm. |
|---|---|---|---|---|---|
| 50 | 17 | 0·0706 | 0·0223 | 0·0221 | 0·0002 − |
| 50 | 17 | 0·0764 | 0·0244 | 0·0239 | 0·0005 − |
| 50 | 17 | 0·1591 | 0·0496 | 0·0499 | 0·0003 + |
| 60 | 17 | 0·1655 | 0·0517 | 0·0519 | 0·0002 + |
| 60 | 17 | 0·1578 | 0·0498 | 0·0494 | 0·0004 − |
| 80 | 30 | 0·1591 | 0·0498 | 0·0499 | 0·0001 + |
| 100 | 30 | 0·3179 | 0·1001 | 0·0997 | 0·0004 − |
| 100 | 30 | 0·3186 | 0·1008 | 0·0999 | 0·0009 − |
| 100 | 30 | 0·3208 | 0·1011 | 0·1005 | 0·0006 − |
| 100 | 30 | 0·3208 | 0·1010 | 0·1005 | 0·0005 − |

From these results it is obvious that the method, which is very rapid, is accurate.

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## ON THE ESTIMATION OF CADMIUM AS THE OXIDE.*

By PHILIP E. BROWNING and LOUIS C. JONES.

In an article entitled "The Estimation of Cadmium" (*Jour. Sci. Chem. Industry*, vol. xiii., 211), Max Muspratt discusses critically some of the methods in use for the

determination of that element. Muspratt finds that the method which involves the precipitation as carbonate, ignition and weighing as oxide, gives low results, and he accounts for these results by the well known tendency of cadmium to reduction, especially in the presence of organic matter. To avoid this reduction he dissolved the precipitated carbonate in nitric acid, evaporated to dryness on a water bath, and gently ignited the nitrate to the condition of the oxide. This treatment also gave low results, although the oxide obtained from the ignition of the nitrate was found to contain traces of sulphate from the solution of the cadmium sulphate used. A second method of treatment was to filter and dry the precipitated carbonate and remove as much of it as possible to a weighed porcelain crucible, ignite and weigh by itself. This oxide was found to be free from traces of sulphate. (Muspratt's theory is that in the ignition of the carbonate the sulphate is dissociated, while the ignition of the nitrate does not effect this result).

The remainder of the cadmium oxide adhering to the paper was dissolved in pure nitric acid, and the solution and rinsings evaporated to dryness and ignited in a weighed crucible and weighed. Here also low results were obtained which, after the extended process of manipulation, would scarcely seem surprising. If, however, Muspratt adds, the oxide obtained from the ignition of the carbonate be taken as Cd₂O the results are satisfactory.

A third modification gives more satisfactory results. The method of treatment is the same as the last mentioned, except that the oxide obtained from the ignition of the carbonate is ignited in a stream of oxygen until no further increase in weight results.

In a former paper from this laboratory (Browning, *Amer. Jour. Sci.*, xlvi., 280), one of us made use of the carbonate method for the determination of cadmium after having separated that metal from copper. The filtration was made on asbestos in a Gooch crucible, and the results were most satisfactory. The object of the work to be described is to show that when the carbonate is filtered upon an asbestos felt previously ignited the dangers of reduction are obviated, and the carbonate process is both simplified and placed among good analytical methods. The solution used for the work was one of cadmium sulphate, and the standard was determined by evaporating measured and weighed portions to dryness in the presence of a few drops of sulphuric acid, igniting at low redness, and weighing as the anhydrous sulphate. The average of several closely agreeing results was taken as the standard. Measured and weighed portions of this solution were diluted to about 300 c.m.³ with hot water and a solution of potassium carbonate, 10 per cent, added drop by drop with constant stirring until no further precipitate was obtained. The precipitate was then boiled for about fifteen minutes, when it became granular and settled quickly. It was then filtered upon asbestos, washed thoroughly, dried, and ignited at red heat until a constant weight was obtained. In several instances the weighed oxide was treated with a drop of nitric acid, again ignited and weighed, but in no case was there a perceptible change in weight. In the accompanying table the results are tabulated.

As will be noticed, the results show a plus error which might naturally be due to a slight inclusion of the alkali carbonate. To test the truth of this hypothesis, a portion of the oxide which gave a plus error of 0·0007 grm. was dissolved and tested for potassium by the perchloric acid method (Kreider, *Amer. Journ. Sci.*, xlix., 443), and an amount of that element was found equal to 0·0006 grm. of the carbonate. Another portion of the oxide which showed no error was similarly treated, and only 0·0002 grm. on the carbonate was found. The results show, as we think, that the carbonate method can be successfully applied to the quantitative estimation of cadmium without recourse to the tedious process of manipulation recommended by Muspratt.

| No. | CdO taken. Grm, | CdO found. Grm. | Error. Grm. |
|---|---|---|---|
| 1. | 0·1140 | 0·1143 | 0·0003 + |
| 2. | 0·1142 | 0·1137 | 0·0005 − |
| 3. | 0·1141 | 0·1148 | 0·0007 + |
| 4. | 0·1141 | 0·1148 | 0·0007 + |
| 5. | 0·1142 | 0·1146 | 0·0004 + |
| 6. | 0·1143 | 0·1147 | 0·0004 + |
| 7. | 0·1143 | 0·1144 | 0·0001 + |
| 8. | 0·1139 | 0·1146 | 0·0007 + |
| 9. | 0·1270 | 0·1272 | 0·0002 + |
| 10. | 0·1279 | 0·1283 | 0·0004 + |
| 11. | 0·1272 | 0·1281 | 0·0009 + |
| 12. | 0·1278 | 0·1281 | 0·0003 + |
| 13. | 0·2556 | 0·2561 | 0·0005 + |
| 14. | 0·2550 | 0·2547 | 0·0003 − |
| 15. | 0·1272 | 0·1279 | 0·0007 + |
| 16. | 0·1281 | 0·1288 | 0·0007 + |
| 17. | 0·1274 | 0·1278 | 0·0004 + |
| 18. | 0·1284 | 0·1290 | 0·0006 + |
| 19. | 0·1271 | 0·1277 | 0·0006 + |
| 20. | 0·1278 | 0·1285 | 0·0007 + |
| 21. | 0·2555 | 0·2555 | 0·0000 ± |

## GENERAL METHOD FOR THE ELECTRO-CHEMICAL PRODUCTION OF METALLIC SULPHIDES.

### By RICHARD LORENZ.

IN like manner, as I have given a general method for the electro-chemical preparation of hydroxides, we may obtain the sulphur compounds of the metals; and here, also, the application of the electro-chemical method has advantages as compared with the chemical method. Whilst in the latter case we have to depend on the acid, neutral, or alkaline character of the solution, by the electro-chemical method we can precipitate any metallic sulphide from a neutral solution, if only it is insoluble in water, without the use of sulphuretted hydrogen or of a metallic sulphide.

For the performance of the experiment, we select a cathode of rod-shaped copper sulphide, and an anode of that metal whose sulphide is to be obtained. The copper sulphide is enfolded in a piece of silk, as there ensues a dissipation of the electrode during electrolysis. As electrolyte, there is used an alkaline chloride, nitrate, or sulphate. The following experiments may be performed :—

Copper as anode, with a cathode of copper sulphide, yields a black precipitate of copper sulphide in a solution of potassium nitrate or chloride.

In the same manner, silver yields in a solution of potassium nitrate a black deposit of silver sulphide. Cadmium forms a yellow deposit of cadmium sulphide.

Tin, in opposition to its electro-chemical precipitation as hydroxide, yields here always the sulphide.

Lead, if precipitated from a solution of potassium nitrate, forms black lead sulphide.

Iron yields, in a solution of potassium chloride, a black precipitate of ferrous sulphide.

Nickel as anode in a solution of potassium chloride, with a cathode of copper sulphide, yields a black deposit of sulphide.

As a matter of course, this reaction may be applied to the production of various other sulphides and will be capable of manifold extensions. In particular, the behaviour of other sulphides as cathodes will have to be considered. In particular, the development of the principle here laid down will be important as regards the electrolytic precipitation of metallic sulphides from aqueous solutions on the application of a sulphide as cathode if it proves possible to fix the ions which appear at the anode. We might thus arrive at an electrolytic method of superseding in the chemical laboratory the nuisance of hydrogen sulphide.—*Zeit. fur Anorg. Chemie*, xii., p. 442.

## THE VALUATION AND STANDARDISING OF SOLUTION OF PERMANGANATE.

### By Prof. Dr. E. RIEGLER.

THE variability of a solution of permanganate necessitates the frequent revision and determination of its value. It is very practical to possess a solution which may be kept without decomposition, and by means of which the value of a solution of permanganate can be determined at any time quickly and accurately.

I prepare such a solution by dissolving 9·9654 grms. chemically pure crystallised oxalic acid in about 500 c.c. water, adding 50 c.c. concentrated sulphuric acid, allowing the mixture to cool, and making up with distilled water to exactly 1 litre.

Each c.c. of this solution corresponds exactly to 0·005 grm. potassium permanganate, according to the equation :—

$$5(C_2O_2H_4.2H_2O) + 2KMnO_4 + 3H_2SO_4 =$$
$$= 10CO_2 + K_2SO_4 + 2MnSO_4 + 18H_2O.$$
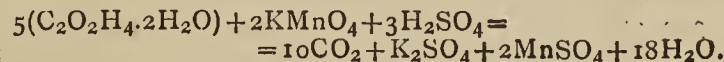
In order to determine the standard of a solution of permanganate we pour from a burette into a small flask exactly 20 c.c. of the above solution of oxalic acid, heated to ebullition, and gradually add (with agitation) from another burette, the permanganate solution in question until the last drop produces a permanent rose colouration. As 20 c.c. of the above solution of oxalic acid correspond exactly to 100 m.grms. of potassium permanganate, we find the weight of this substance in a c.c. of the permanganate solution expressed in milligrms. Dividing 100 by the number of c.c. of this solution, which are consumed until the production of a permanent redness.

If, *e.g.*, there were consumed 25 c.c. of a solution of permanganate, each c.c. of this solution contains $\frac{100}{25} = 4$ m.grms. $KMnO_4$.

I have kept such a solution of permanganate for more than a year without the slightest change.—*Zeitschrift fur Analylische Chemie*, xxxv., p. 522.

## THE REMOVAL OF SILVER AND GOLD FROM SEA-WATER BY MUNTZ METAL SHEATHING.[*]

By A. LIVERSIDGE, M.A., F.R.S., Professor of Chemistry in the University of Sydney.

(Concluded from p. 184).

(g) FROM Newcastle and Hunter River Steamship Company's upper wharf at Morpeth, N. S. Wales. Supposed to have been on piles about four years, exposed to brackish water. Very little corroded.

2000 grains gave—Silver, 5 ozs. 15 dwts. 20 grs.; Gold, 11 grs. per ton. Metallic copper, 62·5 per cent.

(h) From Newcastle and Hunter River Steamship Company's upper wharf at Morpeth, N. S. Wales. Supposed to have been on piles four years in brackish water. Clean, *i.e.*, not coated with green or red scale as usual, and but slightly corroded.

2000 grains gave—Silver, 5 ozs. 7 dwts; Gold, 10·2 grs. per ton. Metallic copper, 62·4 per cent.

(i) From front of pile, No. 1 jetty (between Nos. 4 and 5 cranes), Bullock Island wharf, N. S. Wales. Submerged about twenty years in sea-water. Green, somewhat corroded, but still fairly thick and solid.

2000 grains gave—Silver, 4 ozs. 1 dwt. 16 grs.; Gold, 16·5 grs. per ton. Metallic copper, 61·6 per cent.

(j) From Circular Quay, Sydney, N. S. Wales. Submerged about forty years. The old Tank Stream, now a

[*] Read before the Royal Society of N. S. Wales.

sewer, has its outfall at Circular Quay, but I do not know how near to the samples of sheathing examined. Much corroded, the sheets being eaten into large holes.

4000 grains gave—Silver, 7 ozs. 19 dwts. 18 grs. ; Gold, 6·5 grs. per ton.

The following were treated with sulphuric acid :—

2000 grains gave—Silver, 3 ozs. 17 dwts. 8·4 grs.; Gold, 11·90 grs. per ton.

4000 grains gave—Silver, 4 ozs. 15 dwts. 8·5 grs.; Gold, 8·62 grs. per ton.

Metallic copper, 61·6 per cent. Metallic zinc in the much corroded parts = 34·68 per cent, in the thicker parts 35·49 per cent.

*The scale*, extracted first with 500 c.c. of nitric acid (1—3 aq.) :—

300 grains gave—Silver, 4 ozs. 16 dwts. 11 grs. ; Gold, 4 dwts. 18·5 grs. per ton.

300 grains gave—Silver, 5 ozs. 12 dwts. 19·1 grs.; Gold, 4 dwts. 18·5 grs. per ton.

300 grains gave—Silver, 7 ozs. 10 dwts. 16·5 grs.; Gold, 6 dwts. 1·8 grs. per ton.

260 grains gave—Silver, 6 ozs. 7 dwts. 4 grs. ; Gold, 7 dwts. 18 6 grs. per ton.

150 grains gave—Silver, 12 ozs. 2 dwts. 18·9 grs. ; Gold, 5 dwts. 15·2 grs. per ton.

150 grains gave—Silver, 7 ozs. 10 dwts. 16·8 grs. ; Gold, 10 dwts. 10·8 grs. per ton.

Average, Silver, 7 ozs. 6 dwts. 18 grs. ; Gold. 6 dwts. 13·9 grs. per son.

The loose easily-removed scale of a second lot of sheathing from Circular Quay was assayed, but was first roasted and then extracted with pure sulphuric acid before scorification and cupellation. As will be seen from the results, this scale was richer in silver, the gold was very irregular, and was found to contain platinum derived from the $H_2SO_4$; hence the amounts are omitted. The $H_2SO_4$ had probably taken it up from the platinum stills used in concentrating it.

| | | | |
|---|---|---|---|
| 100 grs. gave—Silver, | 25 ozs. 12 dwts. 5·12 grs. per ton. | | |
| 100 | ,, | ,, | 22 ozs. 17 dwts. 19·84 grs. ,, |
| 200 | ,, | ,, | 23 ozs. 2 dwts. 5·6 grs. ,, |
| 200 | ,, | ,, | 21 ozs. 9 dwts. 13·6 grs. ,, |
| 100 | ,, | ,, | 16 ozs. 1 dwt. 10·56 grs. ,, |
| 100 | ,, | ,, | 18 ozs. 11 dwts. 10·08 grs. ,, |

(*k*) Mr. Hickson forwarded to me a supply of sheathing from the square piles of the original Queen's Wharf, Newcastle, where it had been exposed for probably thirty-five years.

The outer scale, which could be removed by a spatula, was dissolved as usual in pure nitric acid, and the residue scorified and cupelled. Two assays of 150 grains each gave—

2 ozs. 8 dwts. 18 grs. per ton of silver, but no gold.
1 oz. 3 dwts. 11 grs.　　,,　　　　　　　,,

Then 200 grains of the hard and adherent scale under this, with scrapings of the metal itself, gave—

6 ozs. 10 dwts. 16 grs. per ton of silver.
6 ozs. 1 dwt. 12·4 grs.　　　　　　,,

Next the metal sheathing itself, dissolved in sulphuric acid, after removal of the above two scrapings, gave—

6 ozs. 8 dwts. 15·3 grs. of silver per ton.
7 ozs. 4 dwts. 12·4 grs.　　　　　　,,

The amounts of gold are omitted, since the beads were found to contain platinum.

(*l*) Mr. Hickson also forwarded some of the old sheathing from the bottom of the lighter *Topsy*, which was built in 1881, and had been employed at Newcastle.

Two assays were made of the scale from this, and first treated with nitric acid as usual; unfortunately there were only sufficient for 75 grains for each assay. The results obtained were—

Silver, 2 ozs. 3 dwts. 13·2 grs.; Gold, 1 dwt. 17·8 grs. per ton.

Silver, 1 oz. 5 dwts. 6·3 grs.; Gold, 20·9 grs. per ton. The metal dissolved in sulphuric acid yielded—

5 ozs. 4 dwts. 9·5 grs. silver per ton,
5 ozs. 14 dwts. 12·7 grs.　　　,,

The gold is omitted on account of its containing platinum ; but an assay on 1000 grains dissolved in nitric acid gave 5 ozs. 5 dwts. 12 grs. of silver and 15·68 grains of gold per ton.

*Experiments with New Muntz Metal.*

Mr. Darley was also kind enough to have plates of Muntz metal placed for me on the piles of certain wharves, according to the following list, so that they might be examined from time to time, to ascertain whether they really do become richer in gold and silver; each plate was divided as shown by the accompanying diagram, the central strip, 6″ × 14″, was sent to me for assay, and the two other pieces, 21″ × 14″, were placed on a southern and northern wharf respectively, numbered and marked so that they can be readily identified when wanted for examination.

| 14 inches. | 1 foot 9 inches. | 6 inches | 1 foot 9 inches. |
|---|---|---|---|
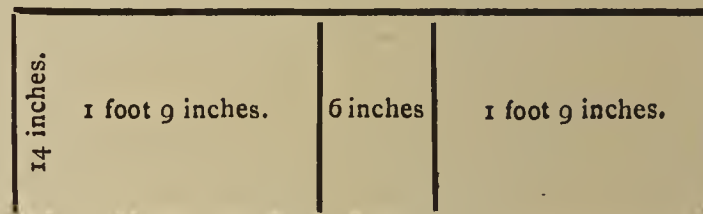
4 feet by 14 inches.

The assays of the new Muntz metal, before exposure to the sea-water, were made for me in the University Laboratory by Mr. S. J Speak, A.R.S.M., Lecturer in Metallurgy and Demonstrator in Chemistry, now of Johannesberg.

They were dissolved in nitric acid (one to three parts water) free from hydrochloric acid : a few drops of hydrochloric acid were afterwards added to precipitate the silver, allowed to stand, then filtered, and the residue scorified with 500 grains of granulated lead and cupelled.

No 1. Richmond River.—Placed on back of fifth pile in middle row from eastern end of Twenty-ton Crane Wharf, south training wall, Ballina, Richmond River. Fixed 1st November, 1893 ; in salt water.

The assay of the new metal gave—

1000 grains gave—Silver, 5 ozs., 1 dwt. 6 grs. ; Gold, 11·8 grs. per ton.

1000 grains gave—Silver, 4 ozs. 19 dwts. 11 grs. ; Gold, 4 grs. per ton.

The trial sheet No. 1, after exposure at Ballina, as above, from November 11th, 1893, to September 30th, 1895, or about twenty months, gave the following results :—

*Scale.*—Consisted mainly of organic matter, 211 grains gave neither gold nor silver.

*Metal.*—Dissolved in sulphuric acid gave—

Silver, 4 ozs. 17 dwts. 19 grs. per ton; Gold contained platinum.

No. 1 a. Moruya. — Placed on the pillar pile of the crane at the town wharf, say 5 miles from the heads. Fixed 11th November, 1893 ; in salt water.

No. 1 a. Moruya—The plate was taken off in October, 1896, after being exposed to the sea-water for twenty-three months, and on assaying it yielded the following results :—Four assays were made, 1000 grains being taken; two of these were first treated with sulphuric acid and the other two with nitric acid, and the residues scorified and cupelled separately.

By sulphuric acid, mean of two assays—Silver, 5 ozs., 11·5 grs.; Gold, 1 dwt. 1·8 grs. per ton.

By nitric acid, mean of two assays — Silver, 4 ozs. 8 dwts. 5·5 grs. ; Gold, 1 dwt. 1 gr. per ton.

It is noticeable that the treatment with nitric acid gives a lower amount than that with sulphuric acid. The scale

from this plate (110 grains) gave no gold, and under 2 ozs. of silver per ton; but as the scale was largely organic matter, and copper oxychloride, much importance need not be attached to the percentage of silver. The inner scale from this (100 grains), treated with sulphuric acid, gave—

Silver, 9 ozs. 4 dwts.. 5·76 grs. per ton; Gold contained platinum.

No. 2. Clarence River.—Placed on No. 4 pile, Yamba Wharf. Fixed 3rd November, 1893, in salt water.

No. 2 a. Shoalhaven River.—Placed on back of second pile, eastern end of public wharf, Nowra. Fixed 31st October, 1893, in brackish water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 6 dwts. 17 grs.; Gold, 16 grs. per ton.

(Dup.) gave—Silver, 11 ozs. 9 dwts. 8 grs.; Gold, 16 grs. per ton.

(Trip.) gave—Silver, 11 ozs. 4 dwts. 2 grs.; 16 grs. per ton.

No. 3. Macleay River.—Placed on front tier of piles at back side of pile from front of Belmore River Wharf, and on second pile on up-stream of wharf. Fixed 20th November, 1893, in brackish water.

No. 3 a. Newcastle.—Placed on No. 5 pile, from west end of Newcastle and Hunter River Steamship Company's upper wharf, Morpeth, at low water spring tides. Fixed 24th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 10 ozs. 10 dwts. 6 grs.; Gold, 10 grs. per ton.

(Dup.) gave—Silver, 10 ozs. 9 dwts. 5 grs.; Gold, 4 grs. per ton.

(Trip.) gave—Silver, 10 ozs. 11 dwts. 8 grs.; Gold, 8 grs. per ton.

No. 4. Richmond River.—Placed on sixth pile from eastern end of middle row of Twenty-ton Crane Wharf, south training wall, Ballina. Fixed 1st November, 1893, in salt water.

No. 4 a. Shoalhaven River.—Placed on back of second pile, eastern end of public wharf, Terrara. Fixed 31st October, 1893, in salt water. The new metal gave —

1000 grains gave—Silver, 6 ozs. 3 dwts. 19 grs.; Gold, 1 dwt. 7·3 grs. per ton.

No. 5. Clarence River.—Placed on No. 3 pile, second row, Iluka Wharf. Fixed 3rd November, 1893, in salt water.

No 5 a. Newcastle.—Placed on third front pile from end of wharf at Pilot Station, Newcastle. Fixed 30th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 12 ozs. 18 dwts. 17 grs.; Gold, 1 dwt. 4·1 grs. per ton.

No. 6. Macleay River.—Placed on fourth pile in second tier, front of Jerseyville wharf, and on front of pile. Fixed 25th November, 1893, in brackish water.

No. 6 a. Shoalhaven River.—Placed on back of corner pile of Government Wharf, Appletree. Fixed Oct. 30th, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 10 ozs. 5 dwts. 3 grs.; Gold, 1 dwt. 7·3 grs. per ton.

No. 7. Richmond River. — Placed on second pile northern end of middle row, Low Level Wharf, Coraki. Fixed 4th November, 1893, in brackish water.

No. 7 a. Newcastle.—Placed on No. 45 pile (front) near No. 11 Hydraulic Crane, Bullock Island. Fixed 30th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 6 ozs. 15 dwts. 10 grs.; Gold, 1 dwt. 2·6 grs. per ton.

Plate No. 7 was taken off on September 25th, 1895, after having been exposed about twenty-three months, and examined with the following results:—

By $H_2SO_4$—Silver, 5 ozs. 19 dwts. 3·8 grs.; Gold, contained platinum.

By $HNO_3$—Silver, 6 ozs. 3·5 grs.; Gold, 1 dwt. 15·2 grs. per ton.

The scale (30 grains) from the plate exposed at Coraki for twenty-three months gave 4 ozs. 13 dwts. 15·5 grains silver per ton; 2 dwts. 4·2 grs. gold per ton, but the amount available, 30 grains only, was so small that the results are of but little value.

No. 8. Newcastle.—Placed on No. 11 pile from west end of Newcastle and Hunter River Steamship Company's wharf, Morpeth, at low water spring tides. Fixed 24th November, 1893, in salt water.

No. 8 a. Moruya. Placed on an iron bark pile (sleeper) western end of Pilot's Main boat-shed at the heads. Fixed 11th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 6 ozs. 7 dwts. 14 grs.; Gold, 1 dwt. 2·6 grs. per ton.

No. 9. Clarence River.—Placed on No. 3 pile, Bush-grove Wharf. Fixed 3rd November, 1893, in salt water.

No. 9 a. Moruya—Placed on centre pile of third pier of Moruya bridge, counting from Mullenderree side. Fixed 11th November, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 10 dwts. 2 grs.; Gold, 1 dwt. 4·1 grs. per ton.

No. 10. Moruya.—Placed on the pile of Pilot's tide-gauge at the heads. Fixed 11th November, 1893, in salt water

No. 10 a. Shoalhaven River.—Placed on the back of third pile from south end of wharf (front row of piles). Fixed 28th October, 1893, in salt water. The new metal gave—

1000 grains gave—Silver, 5 ozs. 18 dwts. 21 grs.; Gold, 15·6 grains per ton.

No. 11. Clarence River.—Placed on second row Lower Southgate Wharf, No. 4 pile. Fixed 3rd November, 1893, in salt water.

No. 11 a. Macleay River.—Placed on second tier of piles from face of Stuart's Point Wharf, on second pile on up-stream side, also nailed on up-stream side of pile. Fixed 18th November, 1893, in brackish water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 19 dwts. 18 grs.; Gold, 1 dwt. 7·3 grs. per ton.

No. 12. Richmond River.—Placed on back of fourth pile, middle row from southern end of High Level Wharf, Coraki. Fixed 4th November, 1893, in brackish water.

No. 12 a. Macleay River.—Placed on middle pile of outside tier and on back of pile from front of Central Kempsey Wharf. Fixed 21st November, 1893, in brackish water. The new metal gave—

1000 grains gave—Silver, 11 ozs. 14 dwts. 5 grs.; Gold, 23·5 grs. per ton.

Only three of the experimental plates have been removed and assayed, viz., No. 1 Ballina, No. 1 a Moruya, and No. 7 Coraki, after an exposure of twenty-three months; the others will be left on for a longer period. In all three cases there was a loss in silver and an increase in the amount of gold.

It is unfortunate that the presence of the platinum in the otherwise pure sulphuric acid was not detected earlier, as I have not the time now to repeat the determinations of gold which had to be rejected on that account; but even without them there are perhaps sufficient assays to settle the question.

The average amounts of gold and silver obtained are—

Twelve specimens of new Muntz metal—Silver, 9 ozs. 4 dwts. 7·6 grs.; Gold, 23 grs. per ton.

Ten specimens of old Muntz metal—Silver, 4 ozs. 13 dwts. 19 grs.; Gold, 16·2 grs. per ton.

Average decrease—Silver, 4 ozs. 10 dwts. 12·6; Gold, 6·8 per ton.

It is not quite satisfactory to have to compare the assays of old specimens of metal with those of new ones, but the old specimens of Muntz metal are not likely to have originally contained less gold and silver than the new,—in fact they probably contained very much more, so that the difference is all the more striking. The assays of the metals from the *Topsy*, this second lot from the

Circular Quay and from Newcastle are omitted from the above because some of them were made with the sulphuric acid afterwards found to contain platinum.

Next the scale from the ten old sheathings gave an average of—

Silver, 5 ozs. 17 dwts. 8 grs.; Gold, 8 dwts. 1·8 grs. per ton.

Or an average increase in round numbers of over 7 dwts. of gold, and an average decrease of 4 ozs. 6 dwts. 23 grs. of silver as compared with the new Muntz metal.

The amount of gold yielded by the old metal and the scale is probably understated, since the chlorides could not be entirely removed from the old metal and they were very abundant in the scale; hence, on dissolving in nitric acid, some of the gold passed into solution as chloride and was lost.

The results do not altogether agree with the previously published views, nor with my own before I commenced the investigation. The silver has not accumulated, but on the contrary decreased; the scale, however, contains a larger amount of gold. The increase of gold in the scale may be due to the deposition of gold from the sea-water on to the surface of the metal, or it may be due to the comparative non-solubility of gold in sea-water; the Muntz metal having been corroded and dissolved away, together with much of the silver, leaving the gold behind; it is probably due to both causes, i.e., partly to deposition and partly to accumulation, for the superficial parts of the experimental plates Nos. 1, 1a, and 7, obtained by scraping them, show an increase in the amount of gold and a decrease in the amount of silver; the increase in the gold cannot in these cases well be due to mere accumulation, since the plates do not appear to have lost sufficient weight to materially increase the proportion of the residual gold.

Under the microscope some of the old sheathings show minute specks of what looks like filmy gold; they may be particles of bright Muntz metal, which have been deposited on the crust of oxychloride, oxide, and other compounds forming the scale, for brass is deposited electrolytically; on treatment with nitric acid they disappeared in the effervescence set up by solution or otherwise—these filmy specks are quite distinct from the points of bright Muntz metal which are seen on the old sheathing, and penetrating, as it were, the scale or crust, and I am inclined to regard them as gold.

As I have pointed out elsewhere, under certain conditions gold is thrown down from very dilute solution by the action of reducing agents, in the form of bright particles or crystals—the amount of gold in such a particle might be extremely small, for $\frac{1}{50000000000}$ grain of gold leaf is visible under the microscope; a piece of corresponding size set free from gold lace would of course be far less in weight. I hope to investigate this matter further, and in the course of another two years it may be desirable to complete this series of experiments by examining the twenty-one plates which have been left on the piles for a longer exposure.

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## REMARKS ON THE SOLUBILITY OF SOLIDS IN GASES.

By HENRYK ARCTOWSKI.

THE conception which we form of "solutions" in general is very comprehensive.

There are solid solutions, liquid solutions, and gaseous solutions; therefore solutions of solids, liquids, and gases in solids, then of liquids in liquids, of gases and of solids in liquids, and we speak also of solutions of gases, or of vapours in gases, of liquids in gases, so that we extend the conception of solutions even to that of solids in gases.

Only liquid solutions have been closely examined; concerning the solid and gaseous solutions we possess as yet only scanty information.

The multiplicity of the mixtures and the combinations, mechanical or chemical, which we include under general rubric of solutions is very extensive. But as we have not yet found any good data for a rational classification of solutions, we must apply the same universal name to all these so heterogeneous bodies.

This generalisation involves, however, a very great disadvantage; that is, we have become accustomed to regard totally distinct things from the same point of view, and consequently to overlook much which is worthy of attention. It is accepted as a postulate that "solutions are mixtures," and this assumption (which we may call a credo) serves as an initial point for considering the phenomenon of solution, and of solutions in all possible cases.

Still this generalisation offers great advantages, for it leads us to seek analogies where apparently only differences are present. It compels us, e.g., to examine one and the same property (or one and the same series of properties), in the three different states of matter which must necessarily lead us to more general comparisons.

Let us take an example. Since the masterly researches of Gay-Lussac on solubility we have not ceased to study quantitatively the solubility of solids, especially of salts in water, and recently we have begun to extend these investigations to other solvents. In consequence of these researches various writers (Nordenskiöld, Le Chatelier, Schröder, and others) have attempted to combine all the results obtained under a simple general law, and I believe I am not mistaken in assuming that hence has arisen the manner of explaining the phenomena of solution and saturation which has found its complete expression in the theory of Nernst. And even if this theory does not strictly agree with the facts in all possible cases, if, on the contrary, the curves of solubility corresponding to the calculated numbers form in one manner an exception, this theory has the enormous advantage over other assumptions that it compels us to think, and throws a light on the track to be followed.

But as there are exceptions, since the laws formulated by Schröder on the one hand, and by Le Chatelier on the other, and which are founded on the assumption that the solutions considered are of a purely physical nature and are correct only in a limited number of cases, we must necessarily assume either that the law is illusory, or that the above assumption is false.

But known facts compel us to presuppose that the hypothesis, according to which all solutions are of a purely physical nature, is erroneous; consequently, the question arises whether, by this fact alone, the law is correct in all possible cases after all physical constants which affect the value of the solubility have been taken into account, and after the elimination of interferences of a chemical nature?

This question cannot be considered at once. But in order in some degree to prepare for the reply, we must—before all things—give account of the nature of such interferences. To this end we must, in my opinion, in the first place turn to simple solutions, and afterwards—still proceeding from the same point of view—examine by degrees more complicated cases. The comparison of the results obtained will permit us to give account of the value and the nature of the interferences, and this will inform us whether the validity of the theory on solubility extends beyond solutions of a purely physical nature.

The "tension of solution" has its quantitative expression in the values of the (molecular) solubility; nevertheless, the curves of solubility in the complicated case of aqueous solution do not correspond at all simply to the rise of temperature (and the heat of solution), and in the case of organic solvents these curves do not seem directly comparable with those of the vapour tension.

In order better to appreciate the individual influence of the different solvents upon the values of solubility, it

seems to me indispensable to append to these determina-tions those of the simplest case (where the part played by the solvent is absolutely null). For this purpose I see only one means, *i.e.*, to dispense entirely with the solvent. In this case the tensions of solution are evidently given by the vapour tension ; and it is exactly the values of the vapour tensions of solid bodies, whose solubility in different solvents we wish to compare, which are as yet totally wanting, the determination of which would be of the highest value for their comparative study.

The property of solids to give off vapours is analogous to their diffusibility in liquids, and therefore to their solubility. The only perceptible difference is this: that in the case just mentioned the physical condition of the matter which acts as a solvent is different, and is in all possible cases without any action upon the dissolved body, since it is a gas, and since, according to Dalton, the mols. of a gas exert neither attraction nor repulsion upon the mols. of another gas.

The sublimation of solids in gases may therefore be re-garded as solution, and it is necessarily a case of purely physical solution.

But instead of perfect gases we may assume as solvents superheated vapours. We may also foresee the case of strongly compressed gases and that of liquids above their critical point. We can consequently pursue this study step by step to liquid state of matter, and thus arrive at the much more complicated case of the solutions ordinary followed.—*Zeitschrift für Anorganische Chemie*, xii., p. 413.

## NOTICES OF BOOKS.

*The Detection and Measurement of Inflammable Gas and Vapour in the Air.* By FRANK CLOWES, D.Sc., F.I.C., Professor of Chemistry in the University College, Nottingham. With a Chapter on the *Detection and Measurement of Petroleum Vapour*, by BOVERTON RED-WOOD, F.R.S.E., F.I.C., Consulting Adviser to the Cor-poration of London under the Petroleum Acts. London : Crosby Lockwood and Son. 1896. Small 8vo., pp. 206.

FREQUENTLY recurring accidents warn us that the re-joicings with which the original safety-lamp for the coal-miner was greeted were somewhat premature. Painful experience has shown that methane—fire-damp—is not the only volatile explosive which is to be dreaded. Prof. Galloway and Sir F. Abel have shown that finely-divided coal-dust may render air explosive in the presence of a minimum of methane—perhaps even in its entire absence. According to Abel, it is not necessary that such dust should be in itself inflammable. In proof of this opinion we may adduce the very serious explosions which have occurred in the large flour mills of Minneapolis in the absence of any inflammable body, gaseous or pulverulent. Hence, in addition to preventing the accumulation of dust in mines, coal-bunkers, &c., it is found necessary in such localities to test the air. How this is to be carried out is the main subject of Dr. Clowes in the work before us. For this purpose the chief and most generally avail-able method is the observation of the " flame-cap." This is " a very pale conical flame surmounting and partly surrounding the upper part " of the flame of a candle or lamp placed in a mixture of air and methane. This cap varies in size and colour according to the proportion of inflammable gas present, as shown in the frontispiece. But the greatest accuracy and delicacy is attained with a hydrogen gas flame burning in a specially-contrived apparatus. The sound test and the electric test are less trustworthy, and the apparatus required is expensive and inconvenient. The hydrogen gas required for testing is introduced into the lamp in a compressed state.

The detection and measurement of carbon monoxide in

the air forms the subject of a separate chapter. The author lays a due weight on the highly poisonous character of this gas, even in small proportions. It is distinctly dangerous if present to the extent of o·2 per cent, and at 1·3 per cent it would undoubtedly prove fatal. Dr. Hal-dane, who has made most valuable researches on the physiological action of this gas, recommends that a man having to enter an atmosphere suspected to contain car-bonic oxide, should carry with him a mouse confined in an open wire cage. If this poisonous gas is present, the mouse will become insensible in about one-twentieth of the time necessary to produce this effect upon a man. He is of opinion that the application of this test would be perfectly legal—a point of which we are by no means certain.

The explosive properties of petroleum vapour are fully explained by Mr. Boverton Redwood, who has made this subject his own.

The work will prove highly valuable to mining engineers, owners and managers of coal mines, and to all persons connected with the storage and transport of petro-leum and its products.

*The Cyanide Process of Gold Extraction.* A Text-book for the Use of Metallurgists and Students at Schools of Mines, &c. Second Edition, Re-written, Enlarged, and Illustrated. By JAMES PARK, Director of the Thames School of Mines, Mining Engineer, F.G.S. (Lond.), Member of the Institute of Mining and Metal-lurgy, late Geological Surveyor and Mining Geologist to the New Zealand Government. Authorised Text book for N. Z. Government School of Mines. Auck-land, N. Z.: Champtaloup and Cooper. Melbourne · G. Robertson and Co.

THIS book is mainly devoted to an account of the McArthur-Forrest process, *i.e.*, the solution of the gold followed up by precipitation with metallic zinc. The reader is cautioned that cyanide solutions, even if very dilute, act energetically upon the copper sulphides, oxides, and carbonates, and the antimony sulphides. Hence if these substances are present, even in small pro-portions, the McArthur-Forrest becomes impracticable, on account of the waste of cyanide. It is also inapplicable to ores in which the gold occurs in a coarse condition. The statement of Gmelin that mercury is not acted on by cyanide is disproved by actual working in New Zealand, *e.g.*, at Waihi. Cyanide is also sometimes wasted by the pre-sence of charcoal and partially carbonised wood. The statement that copper sulphides are not dissolved by cyanide has been fully disproved by the elaborate experi-ments of Prof. Skey. Free sulphur and zinc and lead sulphides are also more or less soluble in cyanide.

We are informed that the problem for the chemist at the cyanide works is to find a practicable method whereby all the sulphur of antimonial and cuprous sulphides can be made to combine with the cyanogen rather than with the potassium of the cyanide. Manganese oxides have been known to occasion an abnormal consumption of cyanide. The strength of cyanide solution which dis-solves a maximum percentage of gold depends on the character of the ore.

The zinc used for precipitating the gold should be free from arsenic and antimony, though a little lead is advantageous.

The Park-Whittaker cyanide process for cupriferous gold ores commences with chlorinisation, the soluble copper chlorides being washed out with water. An alka-line wash is then applied, and finally the gold and silver are extracted with dilute cyanide. The copper is with-drawn from the solution by treatment with scrap-iron.

Other methods for the extraction of gold, not turning on the use of cyanide, are not brought into consideration in this work.

In a concluding chapter cautions are given concerning

the highly poisonous character of the soluble cyanides. Only one fatal case, we are told, has occurred in New Zealand. Solutions of cyanide, if applied to the skin, occasion, in some persons, painful eruptions. From this inconvenience Kaffir workmen are said to be free. It is stated, on the authority of Johann Antal, an Hungarian toxicologist, that a solution of cobalt nitrate is a perfect antidote to cyanide poisoning.

The author, following English and Chinese precedent, has appended to his treatise a series of examination questions.

# CORRESPONDENCE.

## THE SCIENCE AND ART DEPARTMENT.

### *To the Editor of the Chemical News.*

SIR,—The last paragraph of your correspondent " S " in your issue of the 2nd inst. (CHEM. NEWS, lxxiv., p. 174), seems particularly true as indicating what must be the dominating thought of those who dispense the annual grant made by Parliament for distribution among committees in charge of Science classes. I should like to ask why institutions receiving aid of this kind cannot be treated on the same lines as the University Colleges, which receive a lump sum without the detailed enquiries and the great expenses of inspection and examination adopted in other cases. Surely the County Council committees are to be trusted each with a lump sum, seeing that they spend as a rule several times the amount of the grant out of local funds, and sacrifice so much time, thought, and money in providing proper instruction and appliances.—I am, &c.,

C. J. WOODWARD.
Municipal Technical School, Birmingham,
October 12, 1896.

## COTTON SEEDS.

### *To the Editor of the Chemical News.*

SIR,—On page 464 of the third and last edition of Dr. Blyth's admirable work on Poisons, there occurs an article with the heading " Cotton Seeds." The article states that " cotton seeds used as an adulterant of linseed cake, &c., have caused the death of sheep and calves. Cotton seeds contain a poison of which nothing is chemically known, save that it is poisonous; it produces anæmia and cachexia in animals when given in small repeated doses. . . . If, however, the animal has eaten a large quantity of cotton seeds, then there is gastro-enteritis, as well as inflammation of the kidneys."

From the article it is not evident if the editor specifically means whole cotton seeds or cotton seed meal. If used as an adulterant for linseed cake, it evidently refers to cotton seed cake ground, or—as it is called in the United States—cotton-seed meal. The article is probably intended to reier both to whole cotton seed and cotton-seed meal. In either case there certainly must be some mistake in regard to either fresh whole cotton seed or the fresh meal made from the seeds after the extraction of a portion of their oil. Thousands of tons of whole cotton seed are fed annually to the cattle of the southern United States, and there is also an enormous quantity of the meal fed to cattle. The hulls, which are removed from the seed before the extraction of the oil, are also used in enormous amounts in the Southern United States as a feeding-stuff. Not only are cattle fed upon the meal and hulls, but mules and horses also to a limited extent. In Atlanta, Georgia, several thousand head of cattle are fattened each year with the waste cotton seed hulls from the oil mills of that city. These cattle are shipped from Texas to Baltimore on through bills of lading, but are allowed the permission of a stop over of about two months in Georgia to be fattened with this wonderfully cheap material. The cotton seed hulls themselves do not contain enough protein for a proper nutritive ratio. The proper proportion of protein, however, is readily imparted to the cotton-seed hulls by the addition of the meal; and even with this addition of the more expensive meal, the monthly expense of feeding a large animal is only $2.75. The writer has fed a number of Jersey cattle with whole cotton-seed, cotton-seed meal, and cotton-seed hulls without any ill-effects whatever.

Living in the midst of a section feeding enormous quantities of whole cotton-seed and its products, the writer has never yet met with any case which would bear out the supposition that there were any poisonous qualities in this material. In the United States cotton-seed meal is used very largely as an ammoniate for fertilisers, and the pomace from castor-oil beans is also largely used for the same purpose. Castor-oil beans are very poisonous to cattle, the writer having met with several cases where cattle were quickly killed by eating only a few beans which they found lying in the field. It may be possible that the cases that Dr. Blyth refers to might have occurred where the castor-oil pomace and the cotton-seed meal were mixed accidentally, or if intentionally mixed, were so mixed as for fertilising purposes, and the mixture was inadvertently used for feeding animals.—I am, &c.,

GEORGE F. PAYNE, M.D., F.C.S.
Department of Agriculture, State of Georgia,
Laboratory of State Chemist,
Atlanta, Ga., September 24, 1896.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 13, September 28, 1896.

Absorption of the Ultra-Violet Spectrum by Crystalline Substances.—V. Agafonoff.

On a Spectrum of the Kathodic Rays.—M. Birkeland.—These two papers will be inserted in full.

The Existence and the Acid Properties of Nickel Dioxide, Barium Dinickelite.—E. Dufau.—Manganese, cobalt, and nickel all form bioxides having acid functions, yielding with the basic oxides salts whose stability decreases progressively from the manganites to the nickelites.

Researches on the Double Bromides.—Raoul Varet. —A thermo-chemical paper.

Immunity conferred by some Anti-coagulating Substances; Excitement of Phagocytosis; Increase of the Bactericide Power of the Blood.—MM. Bose and Delezenne.—Certain substances, such as the extract of leeches and peptone, if injected into the blood, increase the defensive power of the organism against infections.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Part 3.

Examination of Red Wines for Foreign Colouring Matters.—Albin Belar.—A series of coal-tar pigments can be very simply recognised in red wines by means of nitrobenzol. Most of the coal-tar colours dissolve readily in nitrobenzol, whilst the blue or red pigment of plants—anthakyan—and the similar colouring matter of red wine are absolutely insoluble in nitrobenzol. The detection is effected as follows:—To 5 c.c. of red wine

about an equal quantity of pure nitrobenzol is added in a test-glass. The contents are at first gently shaken; in presence of magenta the nitrobenzol takes at once a bright red colour. If the nitrobenzol remains unaltered, the mixture is shaken more strongly. To remove the emulsion, the mixture is gently heated, when the emulsion disappears. The nitrobenzol collected at the bottom of the test-tube becomes, for some time, perfectly clear and permits of the recognition of the smallest traces of any magenta which may be present. After some trials, it becomes possible to recognise any magenta in the single drops of nitrobenzol which adhere to the sides of the tube after shaking. By using suitable quantities of nitro-benzol, all the magenta can be withdrawn from the red wine, so that a quantitative colorimetric determination can be effected by means of this solvent. A series of other pigments were examined by the same method as to their behaviour with nitrobenzol. The experiments were made first with watery, then with alcoholic solutions, and after-wards Istrian and Dalmatian red wines were mixed with small quantities of the following pigments. The results were alike in each case. From a watery solution of methylen blue, nitrobenzol takes up a part of the colouring matter. The nitrobenzol takes an emerald-green colour. The following pigments are dissolved by nitrobenzol without change of colour:—Magenta, pur-purine (alcoholic solution), and safranine (alcoholic solu-tion). Eosin dissolves with a vinous red, and the solu-tion in nitrobenzol displays no fluorescence. The aqueous part, not dissolved in nitrobenzol, appears yellowish. In rosolic acid, the residual aqueous part, insoluble in nitrobenzol, has a yellow colour. Extract of indigo (sodium disulphindigotate) is quite insoluble in nitrobenzol, and behaves exactly like anthokyan (the blue colouring matter of plants). The experiments on the interesting behaviour of nitrobenzol with various colouring matters are being continued.

**New Bunsen Burner.**—Dr. K. Dierbach.—The con-struction of the new burner cannot be made intelligible without the three accompanying figures.

**Determination of Phenol in Soaps and Disinfec-tive Preparations.** — H. H. Fresenius and C. J. S. Maken.—The determination of phenol in pure aqueous solutions can be easily effected by Koppeschaar's volu-metric method, and its estimation in crude carbolic acid by Tóth's modification of the method of Koppeschaar present no difficulties. Its determination in soaps and disinfectants is in some cases attended with considerable difficulties. Among the methods hitherto applied, that proposed by Charles Lowe (Allen's " Commercial Organic Analysis ") is worthy of notice. A weighed quantity of the soap is dissolved in hot water, and hydrochloric acid is then added until it predominates. The fatty acid set free is then filtered off. The phenol is determined in the filtrate either gravimetrically as tribrom-phenol, or volu-metrically according to Koppeschaar or Tóth. From the experiments quoted, it appears that the proportion of phenol in disinfectants can be determined relatively expeditiously, and with an accuracy sufficient for practical purposes.

**Volumetric Determination of Hydroxides and Carbonates, as well as of Mono- and Bi-carbonates of Alkalis, Alkaline Earths, and Magnesia.**—C. Kippenberger (*Zeit. Angew. Chemie*).—Already inserted.

**Sources of Error in Alkalimetry.**—Fr. Scheiding (*Zeit. f. Angewandte Chemie*).—Already noticed.

**Vacuum Water-bath for Temperatures above 100°.**—J. Baumann and W. Horn.—From the CHEM. NEWS.

**Production of Small Quantities of Ice for Labora-tory Use.**—H. N. Warren.—From the CHEM. NEWS.

**Potassium Biniodate as Ultimate Standard of most extensive Applicability.**—C. Meinecke (*Chem. Zeitung*).—This salt, first proposed by C. von Thon, is met with in trade in a state of extreme purity.

**Borax as an Ultimate Standard for Acids, with Methyl-orange as Indicator.**—C. P. Perman and W. John.—CHEMICAL NEWS.

**Aluminium Amalgam.**—H. Wislicenus and H. Kauf-mann.—This neutral reduction agent is very serviceable for the dehydration of alcohol, ether, &c., as it reacts for water with a formation of hydrogen and aluminium hydroxide. Aromatic nitro-compounds are reduced to amines, or, if the reaction is moderated, to substituted hydroxylamines, sodium nitrite to hydroxylamine, and even to ammonia, &c. In preparing the reagent, alu-minium turnings, freed from oil, are treated with soda-lye until a strong escape of hydrogen occurs; the surface is then rinsed with water and treated for two minutes with a ½ per cent solution of sublimate. These operations are repeated after a short time; the preparation is then quickly washed with water, alcohol, and ether, and the product kept under petroleum ether.—*Berichte.*

**Detection of Small Quantities of Potassium Iodate in Potassium Iodide.**—Spica (*Gazetta Chimica*).—The author's process depends on the sparing solubility of barium iodate and its solubility in hot concentrated hydrochloric acid, from which it can be separated by the addition of water. In this manner 0·002 per cent of potassium iodate can be detected.

**Oxidising Properties of Water Distilled in Copper Vessels.**—Fr. Eschbaum (*Deutsch Med. Wochenschrift*).—Such water, if mixed with normal red blood, shows the spectrum of methæmoglobine.

**Determination of Sugars.**—W. Fresenius and P. Dobriner.—This paper, with its accompanying tables, does not admit either of abstraction or insertion.

**Examination of, and Decision on, Wines.**—W. Fresenius and L. Grünhut.—The same remark must apply to this extensive memoir.

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**Measurement of High Temperatures, especially of the Melting Points of some Inorganic Salts.**—John McCrae (*Annalen der Physik und Chemie*).—The author makes use of a thermo-element of platinum and platinum-rhodium consisting of two wires of 10 c.m. long and 0·2 m.m. in thickness. These were solded together in the flame of detonating gas, and were melted to copper wires at their other end. The copper wires lead to a Quincke multiplier. The electromotive power of the element, corresponding to which a current is generated if the point of contact of the platinum and platinum rhodium wire is heated, and the point of junction with the copper is kept at a constant temperature, is between 300° and 1400° C. proportional to the temperature.

**Contributions to a Knowledge of the Rancidifica-tion of Fats.**—Ed. Spaeth.—The author sums up the results of his experiments as follows:—I. In the rancidifi-cation of fats (hog's lard), which must be regarded as a process of oxidation chiefly occasioned by the action of light and of atmospheric oxygen, the unsaturated body acids (oleic acid) are chiefly attacked with the formation of acids with a low percentage of carbon. There is also a formation of aldehydic bodies and of oxy-fatty acids. II. With the progress of oxidation and the formation of free acids the volatile acids undergo a very great incre-ment. III. All the acids participate in the formation of the free fatty acids. IV. With the increasing oxidation of the fats, their absorptive power, as well as the iodine number, undergoes a corresponding decrease, which diminution is effected by an oxidation and decomposition of the non-saturated fatty acids and by their polymerisa-tion. Such oxidised fats exhibit in the refractometer a decidedly higher deflection than do normal fats. The increase in the deflection is decidedly due to polymerisa-tion of the non-saturated fatty acids. V. Fats which have become rancid have in general a higher melting-point than recent fats.—*Zeit. Anal. Chem.*

## MISCELLANEOUS.

Messrs. Perken, Son, and Rayment announce that their lease of the premises of their Oxford Street branch having lapsed by effluxion of time, that all business will be transacted from their headquarters, 99, Hatton Garden, Holborn Viaduct, E.C.

Farewell Banquet to J. C. Bose.—According to the *Indian Pharmacologist*, a farewell banquet has been given to J. C. Bose, Sc.D., at Bombay, in recognition of his splendid discoveries in electro-chemistry. He is about to visit the laboratories of Britain and the Continent with a view to the enlargement of the laboratory of the Presidency.

University of Aberdeen.—Mr. James Hendrick, B.Sc., F.I.C., Lecturer on Agricultural Chemistry, will deliver his Inaugural Lecture, in Marischal College Buildings, on Friday, 23rd current, at 3 o'clock p.m. Subject: "The Relations of Science to Agriculture." All interested are invited. Those proposing to attend any of the courses may now communicate with Mr. Wilson or Mr. Hendrick.

The British Flint-glass Trade. — It is announced that this country has lost nine-tenths of this important and—until of late—flourishing manufacture. The *Chem. Zeitung* ascribes this disaster in great part to the exertions of the trades' union, which still continues to fight literally against its own bread and butter.

Trades' Unionist Demands.—The recent Congress of Trades' Unions have adopted the following marvellous resolution :—" That this Congress condemns the practice of some railway companies in subjecting their men to scientific tests (for colour-blindness) at the hands of officials incompetent to apply them, instead of practical tests with day- and night-signals. It therefore requests the Committee to approach the Board of Trade with the view of securing the appointment of duly qualified persons to test the accuracy of the men's vision."

ERRATUM.—P. 177, col. 1, line 8 from bottom, *for* " presence " *read* " passage."

## THE ACCURATE DETERMINATION OF OXYGEN BY ABSORPTION WITH ALKALINE PYROGALLOL SOLUTION.*

By Professor FRANK CLOWES, D.Sc. (Lond.).

IT was found repeatedly in my laboratory that during the absorption of oxygen from the Brin gas a considerable volume of carbon monoxide was evolved, although this did not occur in absorbing oxygen from the air. If the evolution of the gas was known to take place, and carbon monoxide was subsequently absorbed by cuprous chloride solution before reading off the residual nitrogen, the estimation of the volume of oxygen was correct; if this precaution was not taken, the estimation was open to serious error. Repeated trials with varying proportions of pyrogallol and potassium hydrate showed that the evolution of carbon monoxide might be entirely prevented by using a sufficiently large excess of potassium hydrate. With the following proportions no fear of this source of error need be felt, even when pure oxygen is being absorbed:—160 grms. of potassium hydrate and 10 grms. of pyrogallol in 200 c.c. of solution. This solution is prepared by dissolving 160 grms. of potassium hydrate in 130 c.c. of water, and then dissolving the 10 grms. of pyrogallol in the alkaline solution.

## CONSTITUTION OF THE MOLECULE.

### By WILLIAM LONGSHAW.

THE object of this article is to attempt to show that in organic chemistry the constitution of the molecule ought to be discussed, from the commencement, by means of spatial representations. The plan adopted by most writers is to start with uniplanar representations; then, after a considerable time, to introduce—when forced by repeated want of agreement between experimental fact and uniplanar representations — van 't Hoft's theory. Moreover, they only adopt it to explain the reactions of compounds whose properties cannot be predicted by ordinary formulæ, and afterwards return to uniplanar representations. That this procedure lays these writers open to the charge of inconsistency is obvious; for if spatial representations must be employed in attempting to exhibit the reactions of substances which contain so-called asymmetrical carbon atoms, &c., it follows that they should be employed consistently throughout the discussion of the constitution of the molecule.

The view of a molecule in terms of the molecular theory, gives great support to the above contention. A molecule consists of a number of atoms which move about together. Since atoms are, by the assumptions of the molecular theory, small particles of matter, these, in the molecule, *must be* arranged in space. Further, the properties of matter compel us to infer that the atoms in the molecule are undergoing certain movements besides those due to the movements of the molecule as a whole. At any particular temperature these movements have a certain intensity; they decrease with the temperature, and at absolute zero they cease to exist. From the above, it follows that any representations which attempt to summarise the properties of substances ought to involve the positions of the atoms in space and their movements.

By examining the origin, mode of development, and uses of uniplanar representations, many reasons are rendered evident why they should be discarded. They have their origin in the fact that one atom of carbon combines with four atoms of a monad element. This fact is graphically illustrated by a representation, as shown—

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$
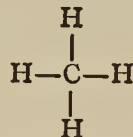
From this fundamental conception has been developed—by methods which have never been explained or justified—other representations, and the following may be taken as skeletons:—

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$
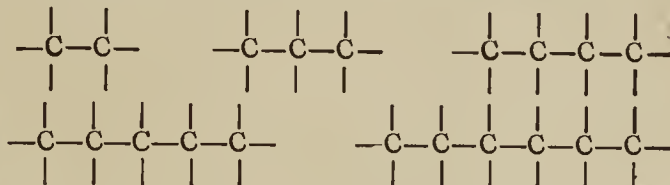
These are the class of "pictures" which figure so conspicuously in the discussion of the constitution of the molecule in our text-books. Therefore, we must point out that ordinary formulæ are excessively vague and indefinite. It has been well said, "that vagueness and incapability of precise proof—or disproof—often enable a false theory to live, and that with those who love truth vagueness should excite suspicion."

Uniplanar representations are employed to predict the number of isomers. When we remember that they fail to do so—(1) when the molecule contains one or more asymmetric carbon atoms, (2) when the molecule contains a double bond, and other conditions, (3) in the ring compounds, &c., &c.,—we must ask by what right are these formulæ employed for this purpose.

From the above, it follows that we cannot employ definite language when discussing ordinary formulæ—undoubtedly a very grave objection to their employment. This fact does not seem to be recognised by some writers. For example, Messrs. Perkin and Kipping, in their "Organic Chemistry," p. 55, say:—"They [viz., ordinary formulæ] express, in fact, in a concise and simple manner the most important chemical properties of the compound." This statement, unfortunately the most important in the book, is not in accordance with fact. This is greatly to be regretted, as it will find its way into the hands of many young students. For, in the first place, ordinary formulæ fail to account for the numbers of isomers known; and therefore they cannot express the reactions of these and allied substances. The above applies to a very large number of compounds.

Not only, however, do ordinary formulæ fail to express the reactions of many compounds, but in some cases they absolutely predict reactions *will not* take place which are *known* to occur. An example of this is afforded by the oxy-acids. The $\alpha$ and $\beta$ oxy-acids do not form a lactone. Their formulæ are—

$$RCH_2CH_2CH_2CHOHCOOH.$$
$$RCH_2CH_2CHOHCH_2COOH.$$
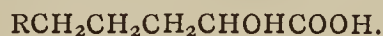
The formulæ of the $\gamma$ and $\delta$ oxy-acids are—

$$RCH_2CHOHCH_2CH_2COOH.$$
$$RCHOHCH_2CH_2CH_2COOH.$$
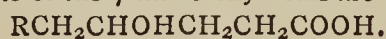
If we attempt to infer from the latter formulæ whether they will form a lactone, bearing in mind the experience gained from the $\alpha$ and $\beta$ oxy-acids, we come to the conclusion they will not. But this conclusion is directly opposed to experimental fact. Almost any number of similar examples can be quoted—so-called straight chain compounds containing four and five atoms of carbon affording the most.

Now, then, let us sum up the objections to the use of

uniplanar representations in the discussion of the constitution of the molecule.

1. They do not take into account the spatial relations of the atoms nor their movements.

2. They are extremely vague.

3. The number of isomers predicted by their means does not, in many cases, agree with fact.

4. They, therefore, cannot express the reactions of many substances.

5. In some cases they predict that certain reactions—which experiment has shown to take place—will not occur.

Surely uniplanar representations of the constitution of the molecule which have the above shortcomings ought not to occupy the prominent position which they do. Ordinary formulæ do undoubtedly throw great light on the properties of substances, and should be retained if we had nothing superior to them. Have we any theory which discusses the constitution of the molecule in a more thorough manner? In van 't Hoff's theory of the position of the atoms in space we have this *desideratum.* We can say in its favour :—

1. That its aim is definite—the position of the atoms in space at the absolute zero.

2. That it predicts correctly the number of isomers.

3. It gives far better summaries of the reactions of substances than ordinary formulæ—see particularly the oxy-acids, compounds containing five and six atoms of carbon, &c., &c.

We can say against it :—

1. It makes no attempt to take into account the movements of the atoms.

2. That its fundamental conception is somewhat vague, and the assumptions involved in its development are undoubtedly not in complete accordance with fact, although sufficiently near the truth to explain the facts which our incomplete experimental inquiry has brought to light. Associated as it is with these important objections, it is in every particular superior to ordinary formulæ.

The above remarks seem to lead to the contention advanced at the commencement of this article, namely, that uniplanar representations ought to disappear from text-books on Organic Chemistry, and spatial respresentation should be used consistently throughout the discussion of the constitution of the molecule.

## BISMUTH OXY-IODIDE.

### By T. R. BLYTH.

WHEN distilling the double iodide of methylamine and bismuth, $(CH_3NH_2HI)_3(BiI_3)_2$, with caustic soda, in order to obtain the methylamine, the residue after distillation was almost white—a fact which could not be understood, as the ordinary subiodide (BiOI) was expected.

On analysis, the compound was found to have the composition $Bi_{17}I_3O_{24}$, or $BiI_3.8Bi_2O_3$, or $3BiOI.7Bi_2O_3$. As this was thought to be a new compound, some bismuth sub-iodide (BiOI) was boiled with caustic soda ; the red colour soon changed to a very slight brown, resulting in the same above compound.

No account has been made of this body before ; in fact, Wurtz says that caustic alkalis and weak carbonates have no action on BiOI. Two other rather complex oxy-iodides of bismuth are mentioned, namely :—

1. Wurtz = $Bi_{14}O_{15}I_{12}$ may be $4BiI_3.5Bi_2O_3$.

2. Watts = $BiI_3.5Bi_2O_3$, or $3BiOI.4Bi_2O_3$, or $Bi_{11}O_{15}I_3$.

This new body ($Bi_{17}I_3O_{24}$) is a light microscopically crystalline powder, having a very slight brown tint, is unattacked by boiling water or alkalis, soluble in dilute hydrochloric acid ; while nitric acid decomposes it, setting free iodine ; sulphuretted hydrogen decomposes it into sulphide,

*Analysis.*

|                          | Found. | Theoretical. |
|--------------------------|--------|--------------|
| Bismuth  .. .. ..        | 82·18  | 82·20        |
| Iodine .. .. .. ..       | 8·85   | 8·84         |
| Oxygen (by diff.) . ..   | 8·97   | 8·95         |
|                          | 100·00 | 99·99        |

ON THE

## EXISTENCE OF SELENIUM MONOXIDE.[*]

### By A. W. PEIRCE.

IT was Berzelius's idea that the odour of decayed cabbage which is noticed when selenium is burned in air is due to the formation of a gaseous lower oxide of selenium which he called the monoxide. The same oxide is said to be formed when selenium sulphide is dissolved in an insufficient amount of aqua regia, in the distillation of a mixture of selenium and selenium dioxide, and in the action of sulphur upon selenium dioxide.

Sacc (*Annales de Chimie et de Physique*, III., xxi., 119) records his inability to obtain such an oxide, and attributes the odour which is noticed under these conditions to a trace of selenium hydride. A very minute trace of the hydride is sufficient to develop a very considerable odour, and traces of moisture may be enough to produce a perceptible odour of the hydride when the conditions are favourable to action upon the elementary selenium. When selenium burns in air, or when its sulphide is oxidised by aqua regia, moisture is inevitably present, and when selenium dioxide is reduced by sulphur or intermixed with elementary selenium its extremely hygroscopic character implies the presence of traces of water.

It has been a generally accepted opinion of late that the selenium monoxide does not exist ; but more recently, in work upon certain organic compounds of selenium, Chabrié has been led to the idea that the monoxide does exist, and that it is a solid body. Chabrié states (*Ibid.*, VI., xx., 273) that when selenium is heated in air it tends to increase in weight. At 100° C. the increase is said to be inappreciable, but at 180° C. it approaches very nearly to the limit corresponding to the formation of the selenium monoxide, SeO. Further, he says that this increase in weight when the selenium is heated to 180° cannot be due to the formation of the dioxide, since that compound, if it were formed, could be seen as a crystalline deposit ; or if the temperature is too high to allow it to deposit, a loss of weight would result. He is so sure of the increase that, were it not for the fact that the monoxide has not been generally recognised, he would suggest, as a possible means for the determination of selenium, to heat it to 180° and estimate it as SeO. The selenium with which Chabrié obtained these results was reduced by acting with sodium sulphite and hydrochloric acid upon the product of oxidation of certain organic compounds of selenium of the aromatic series by means of nitric acid, and filtering on glass wool. The product when dried quickly at 100° gave results in accord with his theory of the constitution of the compounds, counting the selenium dried at 100° as existing in elementary form. Thus :—

|                | I.     | II.    | III.    |
|----------------|--------|--------|---------|
| Se found  .. .. | 0·0347 | 0·0680 | 0·0406  |
| Se by theory .. | 0·0349 | 0·0678 | 0·0414  |
|                | 0·0002 − | 0·0002 + | 0·0008 − |

In other analyses of the same compounds, in which the selenium was dried at 180° instead of at 100°, the

weight of the selenium was so much greater as to suggest the idea that the element had oxidised to the condition of the monoxide. Thus:—

|  | I. | II. | III. | IV. |
|---|---|---|---|---|
| SeO (?) found | 0·0301 | 0·0525 | 0·0523 | 0·0517 |
| SeO by theory | 0·0301 | 0·0517 | 0·0504 | 0·0498 |
|  | 0·0000 | 0·0008+ | 0·0019+ | 0·0019+ |

Had Chabrié actually found that the same identical selenium determined by drying to a constant weight at 100° did actually increase in weight at 180° to a constant amount corresponding exactly to what the weight should be were the monoxide formed, the evidence of such oxidation would be good. What Chabrié did, however, was to show that when the selenium from one sample of his compound was dried at 100° and regarded as elementary selenium, the amount of it found corresponded to his theory of the composition of his compound; while to harmonise the results of analysis with the demands of the theory, when the selenium from another sample of the same preparation was heated to 180°, it became necessary to assume that the selenium had been oxidised to the condition of the monoxide. Moreover, it has been shown very recently, by Krafft and Kaschau (*Ber. d. d. Chem. Gesell.*, xxix., 428), that the composition and constitution given by Chabrié to some, at least, of his organic compounds of selenium cannot be sustained. It has seemed to be desirable, therefore, to put the question of the oxidation of selenium at 180° to the direct test.

I have dried selenium to a constant weight at 100° C., and then have heated it to 180° C. for various periods of time, and in no single case have I observed the slightest increase in weight. In the following table are the results of these experiments. In every case the selenium was taken originally as the dioxide, prepared as described in previous articles, and precipitated in some cases with sulphurous acid, in some instances with potassium iodide, dried to a constant weight at 100°, and then heated to the temperature and for the periods indicated below:—

| Exp. | Se found at 100°. Grm. | Temp. | Time. | Weight. Grm. | Loss. Grm. |
|---|---|---|---|---|---|
| 1. | 0·0356 | 110° | ½ hour | 0·0350 | 0·0006 |
|  |  | 130 | ½ ,, | 0·0348 | 0·0002 |
| 2. | 0·0355 | 110 | ½ ,, | 0·0350 | 0·0005 |
|  |  | 130 | ½ ,, | 0·0347 | 0·0003 |
|  |  | 150 | ½ ,, | 0·0346 | 0·0001 |
| 3. | 0·0576 | 180 | 8⅓ hours | 0·0546 | 0·0030 |
| 4. | 0·0576 | 180 | 8½ ,, | 0·0558 | 0·0018 |
| 5. | 0·3324 | 180 | 2 ,, | 0·3306 | 0·0018 |
| 6. | 0·3500 | 180 | 1½ ,, | 0·3445 | 0·0055 |
| 7. | 0·4274 | 180 | 1½ ,, | 0·4232 | 0·0042 |

Other experiments were made for the purpose of determining if possible just how the losses occur. The selenium, collected as usual upon asbestos in a perforated crucible, was introduced into a large glass tube placed horizontally in an air-bath in such manner that the tube extended outside the bath at both sides and remained cool at the ends. A current of dry air was drawn through ignited asbestos and then through the tube containing the selenium and crucible, and passed to the suction-pump through a glass trap filled with water. A thermometer placed within the tube, and closely adjacent to the selenium, showed the temperature of the selenium as the experiment progressed. On gradually heating the bath no change was observed at first, but at 180° C. a mirror of red elementary selenium formed on the cooler portions of the tube outside the bath, but did not extend so far as the trap. At the end of the heating the crucible was weighed and the loss determined. The washings of the tube and the trap, when acidified and tested with potassium iodide, gave no indication of selenious acid, as would inevitably be the case if selenium dioxide were

formed and volatilised during the heating. The loss is due, therefore, entirely to the volatilisation of the selenium as such.

| Exp. | Se found at 100°. Grm. | Temp. | Time. | Weight. Grm. | Loss. Grm. |
|---|---|---|---|---|---|
| 8. | 0·0706 | 180° | 2½ hours | 0·0628 | 0·0078 |
| 9. | 0·0987 | 180 | 1¾ ,, | 0·0948 | 0·0039* |
| 10. | 0·3192 | 180 | 4 ,, | 0·3121 | 0·0071 |
| 11. | 0·0983 | 180 | 3¾ ,, | 0·0925 | 0·0058 |
|  |  | 200 | 2 ,, | 0·0876 | 0·0049 |

* In current of $CO_2$ instead of air.

In every case, irrespective of the reducing agent employed or details of treatment, I get a loss of weight on heating selenium in air to 180°, due to the volatilisation of the selenium. If this is so, it should be possible to so arrange the apparatus that the selenium volatilised may be caught and weighed.

A drying tube with ground-in stopper was therefore sealed to a smaller tube carrying a bulb filled with ignited asbestos. The selenium was weighed and introduced upon an asbestos felt into the larger tube, and the whole was carefully weighed.

The larger tube was heated in the air-bath, while air was drawn through the tube in the direction of the bulb of asbestos, which was outside the bath and cool. Selenium volatilised as before, very evidently, as far as the asbestos in the bulb, where it was caught. On cooling and weighing the tube and contents, absolutely no change of weight was observed. This shows that no gaseous product is formed to occasion the loss, but that the decrease of weight in the former experiments was due to the volatilisation of the selenium itself.

Thus I am unable to duplicate the results of Chabrié in this matter, although I have followed his method of treatment so far as it is described. The only difference apparent is in the source of the selenium—in this work the dioxide of known purity with which much exact work has recently been done, and in Chabrié's work the oxidation product of certain organic compounds. I fail to see, however, how this difference in origin can affect the sensitiveness of the selenium with reference to the oxidising action of the air.

Having thus been unable to obtain the monoxide in the solid state, I have made some experiments upon the oxidation of selenium by heating it in mixture with the dioxide under such conditions that the existence of a gaseous product, such as Berzelius describes it to be, would be noted, even if it were formed in very small amount.

A hard glass tube of convenient size, about 2 c.m. in diameter and 65 c.m. in length, was washed and dried most carefully and sealed at one end. Through the open end were introduced 0·0247 grm. pure selenium dioxide, freshly prepared and scrupulously protected against moisture, and 0·0250 grm. powdered selenium. The open end was then drawn out in such a way that attachment could easily be made to an air-pump, and an intervening portion of the tube constricted so as to be easily sealed later. The end was attached to a mercury air-pump and the pressure reduced to 4 m.m. By applying a flame to the constricted part the tube was sealed in that condition. The tube was heated gradually in a small combustion furnace until the whole contents were vapourised, maintained in that condition some minutes, and then cooled. At every opportunity of lower temperature the selenium vapours would condense into dark metallic drops which ran into larger and larger drops, like mercury globules, seeming to separate from the dioxide vapours. This treatment was repeated six times at intervals, the contents of the tube showing each time the same phenomena of sublimation and condensation. Nothing was observable at any time to indicate chemical change in either substance, each maintaining the characteristics of its own sublimation.

Finally the air-pump was again attached, and allowed to work until the manometer registered no pressure. Upon breaking the end of the tube by pinching it inside the rubber connector, the height of the mercury column indicated the same pressure as when the tube was originally sealed. When disconnected the tube possessed not the slightest odour.

This experiment was repeated with the sole modification that the heating was not carried to a temperature so high, and this time 0·0730 grm. freshly prepared dry selenium dioxide and 0·0730 grm. powdered selenium were sealed up in the evacuated tube and heated for seven hours at 180° C., and finally for one hour at 200°. Upon breaking the tube under conditions similar to those of the previous experiment, the contents showed no pressure and possessed no odour. Obviously no gaseous product was formed under these conditions.

I have thus been unable to find evidence of the existence of selenium monoxide, either gaseous or solid, and my experience goes to show that the peculiar smell attributed by Berzelius to the monoxide is only developed, as Sacc found, when selenium is heated in presence of moisture, and that a mere trace of moisture is sufficient to produce the odour.

In conclusion I wish to express my thanks to Prof. F. A. Gooch for many valuable suggestions during this work.

## ON THE REDUCTION OF VANADIC ACID BY HYDRIODIC AND HYDROBROMIC ACIDS,

### AND THE

## VOLUMETRIC ESTIMATION OF THE SAME BY TITRATION IN ALKALINE SOLUTION WITH IODINE.*

### By PHILIP E. BROWNING.

THE reduction of vanadic acid from the condition of the pentoxide to that of the tetroxide by the action of hydriodic and hydrobromic acids has been applied to the volumetric determination of vanadium. Holverscheit ("Dissertation," Berlin, 1890) has shown that when a vanadate is treated with potassium bromide and strong hydrochloric acid, and the bromine liberated on boiling is passed into a solution of potassium iodide, the iodine set free and estimated shows the reduction to have gone to the condition of the tetroxide. This method is said to yield most satisfactory results.

Friedheim in a recent paper (*Berichte d. d. Chem. Ges.*, xxviii., 2067, 1895) gives the method favourable comment, and shows also, by a carefully made series of experiments, that the pentoxide may be reduced to the tetroxide by boiling with potassium iodide and sulphuric acid, and, further, that the reduction may be carried even to the condition of the trioxide by substituting for the sulphuric acid strong hydrochloric acid.

In both of the above-mentioned methods the iodine liberated is conducted into a solution of potassium iodide and estimated in the usual manner.

In a former paper (*Zeits. f. Anorgan. Chem.*, vii., 158, 1894) I have shown that vanadic acid may be determined conveniently and rapidly by reducing it to the tetroxide by the action of tartaric acid and estimating it in the residue by direct oxidation with standard iodine after having cooled the solution and having made it alkaline with a bicarbonate. The possibility of applying this method of oxidation to the residue after the reduction with hydrobromic and hydriodic acids led to the series of experiments which it is the purpose of this paper to describe. The advantages of the treatment of the residue are

obvious, and the general method has been applied in a number of methods previously developed in this laboratory. In the first place the complicated apparatus necessary for the distillation and collection of the bromine or iodine is unnecessary, an ordinary boiling-flask or Erlenmeyer beaker being sufficient. In case the distillation process is preferred, the residue may be treated by the method to be described as a control, and the results by both processes allowed to check one another.

For the work to be described solutions of ammonium vanadate were made and standardised by evaporating measured and weighed portions in a platinum crucible to dryness, and igniting in the presence of a drop of nitric acid.

The reduction with hydriodic acid was first tried; the method in general was as follows:— Measured and weighed portions of the vanadate solution were placed in the Erlenmeyer beakers; the amounts of potassium iodide indicated in the tables added from a 10 per cent solution, and finally 10 c.m.³ of a mixture of sulphuric acid and water in equal parts. The contents of the flask was then boiled until the fumes of iodine were no longer visible and the escaping steam gave no indication of free iodine with red litmus-paper (Gooch and Mar, *Amer. Journ. Sci.*, xxxix., p. 300). This point was reached when the volume of the liquid reached about 35 c.m.³. If large amounts of potassium iodide were used the resulting colour was green, owing to the presence of iodine, dissolved in hydriodic acid, with the blue tetroxide of vanadium; if smaller amounts of the iodide were used the resulting colour was blue. The flasks were then removed from the flame, and the contents nearly neutralised by the addition of a solution of potassium or sodium hydroxide,* cooled, and the neutralisation completed with potassium bicarbonate in excess, care being taken to add a few drops of a tartaric acid solution to prevent the precipitation of the tetroxide. To the cooled solution a solution of iodine in potassium iodide was added in slight excess. This point can be quite easily determined, as the iodine is bleached rapidly if the solution is allowed to mix thoroughly as it is drawn from the burette into the flask. After the addition of a distinct excess of the iodine the flask should be closed with a cork coated with paraffin and allowed to stand about one-half hour. It will be noticed that at the end of about fifteen minutes the iodine has ceased to bleach, showing the oxidation to be complete. I have generally allowed the flasks to stand a few minutes longer to be sure of a complete oxidation. The

| | V₂O₅ taken. Grm. | V₂O₅ found. Grm. | Error. Grm. | Amount KI. Grm. | Amount H₂SO₄(1·1) c.m.g. |
|---|---|---|---|---|---|
| 1. | 0·1699 | 0·1690 | 0·0009 − | 1 | 10 |
| 2. | 0·1704 | 0·1699 | 0·0005 − | 1 | 10 |
| 3. | 0·1706 | 0·1700 | 0·0006 − | 1 | 10 |
| 4. | 0·1702 | 0·1692 | 0·0010 − | 1 | 10 |
| 5. | 0·3613 | 0·3620 | 0·0007 + | 1·5 | 10 |
| 6. | 0·1805 | 0·1803 | 0·0002 − | 1 | 10 |
| 7. | 0·3614 | 0·3620 | 0·0006 + | 1·5 | 10 |
| 8. | 0·1811 | 0·1814 | 0·0003 + | 1 | 10 |
| 9. | 0·1807 | 0·1815 | 0·0008 + | 1 | 10 |
| 10. | 0·3613 | 0·3620 | 0·0007 + | 1·5 | 10 |
| 11. | 0·3679 | 0·3674 | 0·0005 − | 1·5 | 10 |
| 12. | 0·3612 | 0·3608 | 0·0004 − | 1·5 | 10 |
| 13. | 0·2893 | 0·2907 | 0·0014 − | 1·5 | 10 |
| 14. | 0·3456 | 0·3448 | 0·0008 − | 1·5 | 10 |
| 15. | 0·3453 | 0·3448 | 0·0005 − | 1·5 | 10 |
| 16. | 0·3907 | 0·3912 | 0·0005 + | 2 | 10 |
| 17. | 0·3908 | 0·3898 | 0·0010 − | 1 | 10 |
| 18. | 0·3906 | 0·3921 | 0·0015 + | 2 | 10 |
| 19. | 0·3909 | 0·3912 | 0·0003 + | 1·5 | 10 |

excess of iodine is then destroyed by standard arsenious acid solution, against which the iodine has been previously standardised, starch added, and the colour brought back with a few drops of iodine. The amount of arsenious acid solution used for the bleaching of the iodine, in terms of iodine subtracted from the whole amount of iodine used, gives the amount of iodine necessary to oxidise the vanadium from the condition of tetroxide to that of pentoxide. The results are given in the table (see preceding column).

The results are on the whole satisfactory, the average error of all the determinations being less than 0·0002−. It will be noticed that large amounts of potassium iodide tend to give plus errors, probably due to the tendency of the hydriodic acid to hold iodine.

The action of the hydrobromic acid was tried in exactly the same manner. It was found that when the residual volume of the liquid in the flask reached 25 c.m.³ the blue colour appeared, and the absence of free bromine was proved by holding a paper moistened with potassium iodide in the steam. If the boiling is not carried to the point indicated, where the blue colour appears, the results come low, showing incomplete reduction. The results follow in the table.

| | V₂O₅ taken. Grm. | V₂O₅ found. Grm. | Error. Grm. | Amt. KBr. Grm. | Amount H₂SO₄(1·1) c.m.³ |
|---|---|---|---|---|---|
| 1. | 0·1890 | 0·1876 | 0·0014 − | 1 | 10 |
| 2. | 0·1886 | 0·1886 | 0·0007 ± | 2 | 10 |
| 3. | 0·1885 | 0·1882 | 0·0003 − | 1 | 10 |
| 4. | 0·1885 | 0·1886 | 0·0001 + | 1·5 | 10 |
| 5. | 0·1881 | 0·1873 | 0·0008 − | 1·5 | 10 |
| 6. | 0·1886 | 0·1882 | 0·0004 − | 2 | 10 |
| 7. | 0·3907 | 0·3894 | 0·0013 − | 2 | 10 |
| 8. | 0·3907 | 0·3903 | 0·0004 − | 2 | 10 |
| 9. | 0·3907 | 0·3894 | 0·0013 − | 2 | 10 |
| 10. | 0·3909 | 0·3889 | 0·0020 − | 2 | 10 |
| 11. | 0·3911 | 0·3903 | 0·0008 − | 1·5 | 10 |
| 12. | 0·3902 | 0·3900 | 0·0002 − | 2·5 | 10 |

Average error of series = 0·0007 −.

## ON THE INVERSION OF SUGAR BY SALTS.*
### No. II.
#### By J. H. LONG.

IN a recent paper (*Journal of the American Chemical Society*, xviii., 120) I have shown that in their behaviour with cane sugar solutions many so-called neutral salts closely resemble weak mineral acids. Salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. The same fact has been pointed out for certain salts by others, notably by Walker and Aston (*Journ. Chem. Soc.*, July, 1895), who determined the speed of inversion of four nitrates, comparing them with dilute nitric acid. This inversion is due to the hydrolysis of the salts in question, the hydrogen of the acids formed being in all cases, probably, the active catalytic agent.

In my former paper I gave some results obtained in a preliminary investigation on ferrous iodide with very strong sugar solutions, and in the present paper I shall give the results obtained with other salts, as well as more extended tests with the iodide.

### Method.

In the experiments before reported I made very strong syrups, containing usually 50 grms. of sugar in 100 c.c., and to these syrups before final dilution weighed amounts of the salts were added, the volume being brought up to

100 c.c. with distilled water. In the following series of tests the amount of sugar present is much smaller, being in all cases 50 grms. in 250 c.c. of the finished solution. This solution is much stronger than is usually employed in inversion experiments, but with many of the salts dissolved weaker sugar solutions could not be well used. The ferrous salts especially require relatively large amounts of sugar to hold them in clear solution, and as many of the experiments given below were made on such salts, it was decided to employ the same weight of sugar in all cases. For each experiment, therefore, 50 grms. of pure sugar was dissolved in water in a 250 c.c. flask by aid of heat. The strong syrup was cooled, and to it was added the salt in the powdered form or dissolved in a little water. After securing a complete solution in either way, it was diluted to the mark and shaken to mix thoroughly.

The syrup so made was poured into small tubes of thin glass for inversion. These tubes held about 20 c.c., and were three-fourths filled. They were cleaned for use by boiling in hydrochloric acid and then in distilled water repeatedly. After having been employed for several series of tests it was found sufficient to soak them twenty-four hours in weak acid, and then in distilled water, rinsing thoroughly finally. After receiving the sugar solutions they were closed with perforated rubber stoppers holding each a short glass tube with capillary opening. The tubes were placed in a receptacle, which was finally immersed in the water of a thermostat holding over 20 litres. The receptacle for the tubes consists essentially of two copper discs, 25 c.m. in diameter, soldered 6 c.m. apart on a copper rod as an axis. The lower disc is furnished with fine perforations, and the upper one with larger openings to receive the tubes. The copper axis below the lower disc ends in a hardened point, resting in a socket, and is extended above to a length of 15 c.m., ending in a grooved pulley around which a belt passes. Power applied to this belt rotates the tube receptacle, which at the same time keeps the water of the thermostat in motion. The thermostat itself consists of a large copper oven covered with asbestos boards on five sides. The top has perforations for the temperature regulator, thermometer, and rotating axis of the tube receptacle. A section of the top can be quickly removed to take out tubes, but at other times should be left closed to exclude light. The capillary tubes in the stoppers closing the inversion tubes project about 2 c.m. above the water.

With the apparatus employed it was possible to maintain a constant high temperature with a little watching through ten hours. A temperature of 85° was held with variation of less than 0·1° in either direction. With many salts the rate of inversion is exceedingly slow at ordinary temperatures, in fact almost imperceptible. For convenience in working, therefore, it was found necessary to invert at a high temperature, and 85° was chosen. In a few instances a slightly higher temperature was employed, but the results obtained are not included below.

The reaction between the sugar and salt is probably in most instances analogous to that between sugar and weak acids, and the rate of inversion may therefore be expressed by the same differential equation—

$$\frac{dx}{dt} = K(A - x).$$

The integration of this for $t$ and $x = 0$, together, leads to the well known formula—

$$K = \frac{1}{t} \text{ nat. log. } \frac{A}{A - x},$$

where A represents the amount of sugar present at the beginning of the inversion, $x$ that inverted at any time, $t$ of an observation, and K the "constant" or "co-efficient" of inversion.

As the reaction is most easily followed by means of the polaristrobometer, A is conveniently measured by the total change in rotation which is observed between the

beginning of the reaction and after complete inversion. $x$ is measured by the change of rotation from the beginning up to the time, $t$, of any observation. For convenience common logarithms are employed in all the calculations below. As the sugar solutions were mixed with the inverting substances at a low temperature, the intervals, $t$, could be reckoned only from the time when the mixtures in the tubes had reached the constant temperature of the experiment. Preliminary tests were therefore made to determine several points of practical manipulation. The thermostat was first brought to a temperature of about 87—88°, and the filled experimental tubes and their receptacle immersed in it. From this a fall of temperature resulted, because of the low temperature of the solution. In five or six minutes the constant temperature of 85° was reached, and by regulation of the gas flame this was maintained. In another set of experiments it was found that the solutions in the experimental tubes could be brought to a temperature of 85° from the room temperature in four to six minutes. It appeared, therefore, that ten minutes was amply sufficient time to allow, after introducing the tubes into the thermostat, before beginning the actual observations, and this was done in all cases in the experiments given below. In the case of bodies which invert but slowly there is little objection to the loss of this first ten minutes of the reaction, but in a few instances it was found to be a decided drawback, as will be seen below.

Usually 250 c.c. of the solution was prepared for experiment, and this was filled into fifteen or sixteen tubes, and put into the thermostat. At the end of ten minutes a tube was withdrawn and cooled very quickly by immersion in cold water, or by holding it under a flowing hydrant. The contents were then poured into a polarisation tube and polarised at the constant temperature of 20° in most cases. In a few tests made in warm weather a temperature of 25° was maintained in the dark room and in the water flowing around the observation tube. This first observation gives the initial rotation, and the time of removing the tube may be put as $t=0$, Tubes were removed at different intervals following and treated in the same manner. The results of the polarisations were always very constant during the first few hours heating in the thermostat, as was found by removing and polarising the contents of three tubes, but after five or six hours less regular results were found, and I adopted the plan of taking the mean result obtained by examining two or three tubes. With fifteen or sixteen tubes I made observations at eight or nine intervals.

After polarising the liquids in the last tubes removed, the contents were mixed, returned to a tube and heated longer to obtain the end point of the reaction, that is, the point of complete inversion. The point found in this manner does not always agree with that calculated from the known weight of pure cane sugar in the original solution. Even with dilute acids the phenomenon of inversion is not as simple a thing as usually represented. As shown by Gubbe (*Ber. d. Chem. Ges.*, xviii., 2207) and others, the specific rotation of invert sugar depends not only on the concentration, but on the time, temperature, and acid used. Prolonged heating with salts produces in many cases, apparently, a slight decomposition of the levulose, from which the negative rotation of the invert sugar is found smaller than it should be theoretically. In a few instances, however, the negative rotation of the invert sugar was increased. From the experiments of Gubbe it may be calculated that 50 grms. of cane sugar in 250 c.c. would yield a solution after inversion, which in a 200 m.m. tube should show a negative rotation of −8·6°. The rotation observed in my experiments was usually about −8·3°, but an accurate determination was not always possible, as some of the solutions became slightly coloured before inversion was quite complete, and in other cases a negative rotation once observed seemed to grow slightly less on longer heating, making the exact end point somewhat uncertain. The discrepancies were not

large in any case, however, and I decided to take −8·3° as the true end point for the 200 m.m. tube, and −4·15° for the 100 m.m. tube.

With some of the salts examined the velocity coefficient, K, is practically constant, with others it increases with the time, while in still other cases it decreases.

The sugar used in all the experiments was crystallised cut loaf of high degree of purity, and selected for the purpose. With 50 grms. in 100 c.c. it yields a solution of almost perfect clearness, which can be easily polarised in a 400 m.m. tube. Weaker solutions yield, on inversion, results which agree perfectly with the theoretical requirement.

(To be continued).

# ON THE ABSORPTION OF THE ULTRA-VIOLET SPECTRUM BY CRYSTALLINE SUBSTANCES.

## By J. AGAFONOFF.

HAVING had in view a qualitative study rather than measurements, properly so-called, I have been able to content myself with a very simple experimental arrangement. As the source of light I took a strong induction spark striking between cadmium electrodes. A lens of quartz of a short focus collected the rays on the slit of a large spectrometer provided with achromatic lenses of quartz and fluor-spar, a prism of fluor-spar, and a small photographic camera instead of an eye-piece. A Rochon prism of quartz without Canada balsam was installed between the collimator and the prism. We obtain thus, at the focus of the spectrometer, two spectra placed one above the other, and polarised at right angles. The crystal to be studied was fixed on a vertical graduated circle quite near the slit of the collimator; it was applied against a small hole pierced in the centre of the circle and forming a diaphragm. We could thus cause the crystalline plate to rotate in its plane and modify its azimuth with reference to the principal sections of the Rochon, without the region traversed by the rays undergoing the least change.

I have studied about 130 crystalline substances. Two only—tourmaline and hæmamellitic acid—have shown polychroism in the ultra-violet part of the spectrum.

In the other substances the two spectra polarised at right angles presented no appreciable difference in this region. The absorption of the ultra-violet began at the same ray for plates cut out of one and the same crystal according to different orientations. The position of the limit depended very little on the thickness of the plate within the limits (naturally very restricted, 0·5 m.m. to 1 c.m.) in which I was obliged to operate.

Isolated absorption bands in the spectrum are very rare. I have observed such only in the following salts :—

*Magnesium sulphate* with $7H_2O$ ; absorption between the rays Cd 18 and Cd 24 (Mascart's rotation).

*Nickel and ammonium sulphate* with $6H_2O$ ; absorption between 7 and 9, and between 18 and 23.

*Ammonium alum* ; absorption between 18 and 23.

*Nickel nitrate* at $6H_2O$ ; absorption between 6 and 9.

*Potassium nitrate ;* absorption between 12 and 17.

We recognise at once the preponderant influence exerted upon absorption by the chemical nature of the molecule. The results which we have obtained for crystals present a remarkable agreement with those which C. Miller and J. L. Soret have obtained for saline solutions. Like these authors, we find that the sulphates are very transparent; the majority transmit the entire spectrum of cadmium; only copper and didymium sulphates absorb the rays more refrangible than Cd 17 and Cd 18 respectively; thallium alum transmits as far as Cd 18 inclusively.

The chromates absorb all the ultra-violet, and, further,

the violet and the blue. In general the presence of chrome increases absorption. Thus potassium chlorate transmits as far as Cd 24, whilst the chloro-chromate, $KClCO_3$, absorbs the blue, violet, and ultra-violet. Neutral potassium oxalate transmits as far as Cd 16; chromium-potassium oxalate only as far as Cd 14.

The nitrates absorb much more than the sulphates; that of aluminium from Cd 13, that of potassium from Cd 19, and that of potassium and nickel from Cd 13.

Among seventy organic crystals which I have studied, only six transmit rays more refrangible than Cd 17; tartaric acid up to Cd 18; potassium tartrate up to Cd 23; mercury cyanide up to Cd 18; erythrite up to 26. The great transparency of crystals of erythrite is quite in accordance with Miller's observations on sugars in solution. In general the limit of absorption of the ultra-violet by organic crystals lies between Cd 9 and Cd 12. Many coloured compounds aborb all the ultra-violet. The derivatives of thymoquinone are highly coloured and polychroic, and all of them entirely absorb the ultra-violet spectrum.

The strong absorption of the organic bodies seems to indicate that the more complicated chemical molecules tend to absorb more abundantly the ultra-violet rays. We may further observe that nearly all the substances which have a strong absorption crystallise badly (except the chromates) ; on the contrary, the substances which crystallise well are in general transparent—such as the alums, quartz, fluor-spar, the sulphates, and, among organic substances, the tartrates, citric acid, and erythrite.

This remark, however, requires to be confirmed by more numerous observations.

Hæmamellitic acid and tourmaline, as we have seen, are polychroic in the ultra-violet. I have studied the tourmalines from different localities. The two spectra separated by the Rochon prism are distinctly different if we take care to direct the tourmaline in such a manner that one of the spectra is formed by the ordinary ray, and the other by the extraordinary ray. The ordinary ray is absorbed in its visible portion and partly tranemitted into the ultra-violet, whilst the inverse holds good for the extraordinary spectrum. An analogous reversal is observed with hæmamellitic acid.—*Comptes Rendus*, cxxiii., No. 13.

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## INDUSTRIAL ACCIDENTS IN GERMANY
### FOR THE YEAR 1895.

*Province East Prussia.*—There were 1327 accidents, 16 of which proved fatal.

*West Prussia.*—1565 accidents, 10 fatal.

*Potsdam.*—2764 accidents, 25 fatal.

At the aniline works at Rumburg a workman died of arsenic poisoning, arsenic hydride having been evolved.

*Frankfurt-on-Oder.*—There were 2017 accidents, 28 of which proved fatal. At an explosives works a man died from inhaling nitrous vapours.

*Berlin and Charlottenburg.*—Accidents 5010, being 723 more than in the former year. Twelve fatal. One death was occasioned by inhaling vapour of carbon disulphide. At the Berlin Gas-works a man died with symptoms of heat stroke on leaving the retort-house. The number of cases of lead-poisoning in the accumulator-works was very high.

*Pomerania.*—2107 cases, 22 fatal. In Posen, 1509 accidents, 37 fatal, chiefly at sugar-works.

*Breslau.*—3254 accidents, 35 fatal. Five men were taken ill after clearing out a Glover tower, and one died. The state of health at the white-lead works is very unfavourable. At the great arsenic works there were no accidents.

*Liegnite.*—20 fatal accidents.

*Oppeln.*—5504 accidents, or 354 more than in the previous year.

*Magdeburg.*—3694 accidents, 23 fatal.

*Merseburg.*—2011 accidents, 19 deaths. Increased precautions have been adopted in the traffic with liquid carbonic acid. A man was killed whilst thawing frozen dynamite, and two others were injured. The " paraffin itch " seems to be disappearing. No special diseases have been observed at the chrome-works.

*Erfurt.*—748 accidents, 8 fatal.

*Slesvic.*—2906 cases. Twelve soldiers died from the explosion of a torpedo-boat. At a tannery there occurred two cases of splenic fever, one of which proved fatal. At a metal-work a man died from phophorus-necrosis.

*Hanover, Stade, Osnabrück, and Aurich.*—3522 accidents. A severe explosion took place at a manure-works during the extraction of fat from leather waste. The assumed safety of glass lamps against fire is called in question.

*Münster.*—Accidents, 837 cases, *i.e.*, 20 per cent more than in the previous year; 38 of the accidents proved fatal.

*Minden.*—712 cases. An explosion took place at a glass-works; the cause doubtful. One man was killed and two severely injured.

*Arnsberg.*—8653 accidents, 83 of which proved fatal. At the ammonia-works at Bulmke a boiler exploded. Two men died the same night from the burns.

*Cassel.*—1059 cases, 9 fatal. Six cases of splenic fever occurred at a work for weaving horse-hair, one of which proved fatal. No cases of phosphoric necrosis have been announced, but two seem to have been kept secret.

*Wiesbaden.*—2306 cases. A workman entered an apparatus before it had been freed from poisonous gases, and was suffocated. Two workmen perished by burning in a lacquer-works, from neglect of orders. At a chemical-works anilism becomes frequent in summer during the preparations of benzene and toluene. Lead colic occurred at lead-works and at accumulator-works.

*Coblentz.*—796 cases as against 736 the previous year; 14 fatal.

*Dusseldorf.*—Accidents 13,324, deaths 61. At a blue-dye-works a man fell into a tank of chromic acid, and died in consequence. A man at another works fell into a boiling dye-pan. At a work where chrome lyes were regenerated chrome ulcers occurred in considerable number. At a chemical work where nitrobenzene was manufactured there occurred serious symptoms of disease, such as fainting, dizziness, and paralysis.

*Cologne.*—Cases 3648, deaths 41.

*Trier.* — 2291 cases, deaths 27. Mischief was occasioned by the dust of Thomas and Gilchrist slags.

*Aachen.*—1973 cases, deaths 18. Lead diseases occurred in the metallurgical establishments.

The laws enacted to restrict the employment of young boys and girls have done more harm than good. The children are now made to work at home on very low wages.—*Chemiker Zeitung.*

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## ACTION OF LIGHT UPON DYED COLOURS.*

DURING the past year (1895-96) the work of this Committee has been continued, and a large number of wool and silk patterns, dyed with various natural and artificial *blue* and *green* colouring matters, have been examined with respect to their power of resisting the fading action of light.

The general method of preparing the dyed patterns, and the manner of exposing them under glass, with free access of air and moisture, were the same as already adopted in previous years.

The thanks of the Committee are again due to James A. Hirst, Esq., in whose grounds the patterns were exposed at Adel, near Leeds.

Each dyed pattern was divided into six pieces, one of which was protected from the action of light, while the others were exposed for different periods of time. These "periods of exposure" were made equivalent to those adopted in previous years by exposing, along with the patterns, special series of "standards," dyed with the same colouring matters as were then selected for this purpose. The standards were allowed to fade to the same extent as those which marked off the "fading period" in previous years, before being renewed or before removing a set of dyed patterns from the action of light. The patterns exposed during the past year are therefore comparable, in respect of the amount of fading action to which they have been submitted, with the dyes already reported upon.

The patterns were all put out for exposure on July 19, 1895, certain sets being subsequently removed on the following dates:—August 12, September 3, September 20, 1895; April 1, July 9, 1896. Of these five "periods of exposure" thus marked off, periods 1, 2, 3 were equivalent to each other in fading power, whereas periods 4 and 5 were each equivalent to *four* of the first period in this respect; hence five patterns of each colour have been submitted respectively to an amount of fading equal to 1, 2, 3, 7, and 11 times that of the first "fading period" selected —viz., July 19 to August 12, 1895.

The dyed and faded patterns have been entered in pattern-card books in such a manner that they can be readily compared with each other.

The following tables give the general result of the exposure experiments made during the year 1895-96, the colours being divided, according to their behaviour towards light, into the following five classes:—Very fugitive, fugitive, moderately fast, fast, very fast.

The initial numbers refer to the order of the patterns in the pattern books. The S. and J. numbers refer to Schultz and Julius's "Tabellarische Uebersicht der künstlichen organischen Farbstoffen."

In the case of colouring matters requiring mordants, the particular mordant employed is indicated in brackets after the name of the dye-stuff.

CLASS I.—VERY FUGITIVE COLOURS. (WOOL).

Many of the colours of this class have faded so rapidly that at the end of the first "fading period" (July 19 to August 12, 1895) only a very faint colour remains, and at the end of the fifth period (one year) all traces of the original colour have disappeared, the woollen cloth being either white or of a yellowish or greyish appearance.

*Triphenylmethane Colours.*

Wool Book IX.
*Basic Colours.*—
10. Victoria Blue R. Constitution not published.
11. New Victoria Blue B. Constitution not published.
12. Victoria Blue B. Hydrochloride of phenyl-tetra-methyl - triamido - diphenyl-α-naphthyl - carbinol. S. and J. 274.
13. Night Blue. Hydrochloride of p-tolyl-tetra-ethyl-triamido-diphenyl-α-naphthyl-carbinol. S. and J. 275.
14. Victoria Blue 4R. Hydrochloride of phenyl-penta-methyl - triamido - diphenyl-α-naphthyl-carbinol. S. and J. 276.

*Safranine Colours.*

*Basic Colours.*—
24. Neutral Blue. Phenyl-dimethyl-p-amido-pheno-naphthazonium chloride. S. and J. 354.

*Oxazine Colours.*

*Acid Colours.*—
9. Gallanilic Indigo PS. Sulphonated product of the action of aniline on gallocyanine-anhydride-anilide.

24. Fluorescent Blue. Ammonium salt of tetra-brom-resorufin.
*Basic Colours.*—
5. Capri Blue GON. Dimethyl-tolyl-ammonium-dimethyl-amido-phenoxazine chloride.
7. Cresyl Blue 2BS. Dimethyl-tolyl-ammonium-amido-phenoxazine chloride.
19. Nile Blue. Dimethyl-phenyl-ammonium-α-amido-naphthoxazine chloride. S. and J. 344.
20. New Methylene Blue GG. Dimethyl-phenyl-ammonium - dimethyl - amido - naphthoxazine chloride.

*Thiazine Colours.*

*Basic Colours.*—
3. Thionine Blue GO. Zinc double chloride of diethyl-dimethyl-thionine.
4. Methylene Blue B. Zinc double chloride of tetra-methyl-thionine.
8. Gentianine. Hydrochloride of dimethyl-thionine.
9. New Methylene Blue N. Hydrochloride of diethyl-toluthionine.
—. Toluidine Blue. Zinc double chloride of dimethyl-tolu-thionine. S. and J. 351.

*Azo Colours.*

Wool Book X.
*Direct Cotton Colours.*—
1. Diamine Sky Blue. From diphenitidine and amido-naphthol-disulphonic H.
2. Chicago Blue 6B. Constitution not published.
3. Brilliant Benzo Blue 6B. Constitution not published.
8. Diamine Blue 6G. Constitution not published.

*Notes.*—Certain colours in this class—*e.g.*, Gentianine, &c.—fade during the first period to a grey colour possessing a moderate degree of fastness. Neutral Blue is characterised by fading to a dull reddish colour. Gallanilic Indigo PS and Diamine Blue 6G, when completely faded, leave the wool of a pronounced yellow tint.

CLASS II.—FUGITIVE COLOURS. (WOOL).

The colours of this class show very marked fading at the end of the second "fading period" (August 12 to September 3, 1895), and after a year's exposure they have entirely faded, or only a tint remains.

*Triphenylmethane Colours.*

Wool Book IX.
*Basic Colours.*—
1. Turquoise Blue, Constitution not published.
2. Turquoise Blue 2B. Constitution not published.
6. Glacier Blue. Zinc double chloride of dichlor-dimethyl-diamido-ditolyl-phenyl-carbinol.

*Acid Colours.*—
5. Cyanol extra. Sodium salt of *m*-oxy-diethyl-diamido-phenyl-ditolyl-carbinol-disulphonic acid.

*Thiazine Colours.*

10. Thiocarmine. Sodium salt of diethyl-dibenzyl-thionine disulphonic acid.

*Oxazine Colours.*

*Basic Colours.*—
27. Muscarin J. Dimethyl-phenyl-p-ammonium-β-oxy-naphthoxazine. S. and J. 343.
28. Metamine Blue B. Dimethyl-phenyl-p-ammonium-β-naphthoxazine. S. and J. 342.
29. New Fast Blue H. Constitution not published.
30. New Fast Blue F. Constitution not published.
*Acid Colour.*—
27. Azine Blue. Constitution not published.

*Safranine and Induline Colours.*

*Basic Colours.*—
15. Basle Blue B. Dimethyl-amido-tolyl-amido-tolyl-pheno-naphthazonium chloride.

16. Diphene Blue R.   An induline colour.
17. Indazine M.   Tetra-methyl-diamido-diphenazine-phenyl-chloride.   S. and J. 364.
26. Metaphenylene Blue B.   Tetra-methyl-di-*o*-tolyl-diphenazonium chloride.

### Natural Colouring Matters.
Acid Colours.—
1. Indigo Carmine.   Sodium salt of indigotin-disulphonic acid.
2. Indigo Purple.   Sodium salt of indigotin-monosulphonic acid.

(To be continued).

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## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

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To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
*Water Examiner, Metropolis Water Act,* 1871.

London, October 8th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Sept. 1st to Sept. 30th inclusive.  The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were found to be clear, bright, and well filtered.

The rainfall in the Thames Valley during the month of September has been excessive, amounting to no less than 5·47 inches.  The 30 years' average rainfall for September being 2·43 inches, there is an excess of 3·04 inches.  This large amount has not, however, brought up the year's supply to the normal point; the deficiency for the nine months of 1896 being still 2·93 inches.

It will be of interest to compare the chemical composition of the Thames-derived waters for this September with that for the corresponding month last year; September, 1895, having been one of the driest, and September, 1896, one of the wettest on record.

Comparison of the Averages of the Five Thames-derived Supplies for the Months of September, 1895 and 1896.

Rainfall, Sept., 1895 .. .. 0·57
    ,,      ,,   1896 .. .. 5·47

| Common Salt. Per gall. Means. | Nitric Acid. Per gall. Means. | Hardness. Degrees. Means. | Oxygen. reqd. Per gall. Means. | Organic Carbon. Per gall. Means. | Organic Carbon. Per gall. Max. | Colour. Br'n:Blue. Means. |
|---|---|---|---|---|---|---|
| Sept, | | | | | | |
| 1895. 1·980 | 0·685 | 12·97 | 0·032 | 0·081 | 0·098 | 10·4 : 20 |
| 1896. 2·228 | 0·834 | 13·41 | 0·048 | 0·087 | 0·146 | 14·0 : 20 |

In spite of the fact that the organic impurities in a river water are likely to be much higher in a dull wet season than in a bright dry one, the purification resulting from large storage or impounding reservoirs, combined with filtration, is so effectual that the influence of the very exceptionally wet and sunless month is scarcely to be noticed, the organic carbon, which may be regarded as the measure of organic matter present, being only increased in the third place of decimals.

The bacteriological results are shown in the following table :—

| | | Colonies per c.c. |
|---|---|---|
| Thames water, unfiltered .. .. .. .. .. | | 1331 |
| Thames water, from the clear water wells of the five Thames-derived supplies.. | highest | 40 |
| Ditto      ditto      .. .. .. .. | lowest | 3 |
| Ditto      ditto      .. (12 samples) | mean | 11 |
| New River water, unfiltered .. .. .. .. | | 709 |
| New River water, from the Company's clear water well .. .. .. .. .. .. .. | | 4 |
| River Lea water, unfiltered   .. .. .. .. | | 1642 |
| River Lea water from the East London Company's clear water well .. .. .. .. .. | | 14 |

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

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## NOTICES OF BOOKS.

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*Applied Bacteriology.*  An Introductory Handbook for the Use of Students, Medical Officers of Health. Analysts, and others.  By T. H. PEARMAIN and C. G. MOOR, M.A., Cantab., Members of the Society of Public Analysts, Associates British Institute of Public Health, &c.  8vo., pp. 360, with 8 plates and 81 figures.  London : Baillière, Tindall, and Co.  1896.

IN the very face of a writer who asserts in the columns of an esteemed medical contemporary that "the whole modern doctrine of bacteriology is a gigantic mistake," we must venture to pronounce this work a timely and useful contribution to our hygienic literature, and to offer to the authors our warmest congratulations.

We find here in the first place an account of the history of bacteria, and of their place in nature.  It is a most fortunate circumstance that they are proved to be plants and not animals, as otherwise their study would have been denounced as "vivisection."  Our knowledge of these minute beings is traced back to Anton Leuwenhoeck, of Delft, who, about 1675, constructed a microscope sufficiently powerful to demonstrate their presence in water, saliva, &c.  About a century later Spallanzani discovered the method of sterilising specimens and apparatus by means of heat.  In 1830 Ehrenberg made a further advance in their study, and was followed by Cohn, Schwann, and Dusch.  But the illustrious Pasteur must be considered as the creator of the modern science of bacteriology.  To him we owe the final disproof of the erroneous doctrine of "abiogenesis," otherwise known as spontaneous generation.  Subsequently we have witnessed a series of discoveries, although very much still remains to be done and to be established beyond the reach of controversy.  It must be remembered that the study of bacteria—using the word in its most general sense—does not alone concern the physician.  It is of high interest in chemistry, both pure and applied.  Among the startling facts here mentioned we find that the descendants of a single bacillus, if allowed to multiply unchecked, would after three days reach the weight of 7,366 tons.

The bacteria are here arranged in four main divisions: Coccaceæ, Bacteriaceæ, Leptotricheæ, and Cladotrichiæ,

Another division of the bacteria turns on their vital conditions, as pointed out by Pasteur. Some, the aërobic species, require the presence of air or of compounds giving off oxygen. Others, the anaërobic forms, can grow in the entire absence of oxygen, and some, indeed, cannot tolerate its presence.

The range of temperature at which they can exist is very wide. Some can grow at 0°, whilst others can increase at 60° to 70° For any object to be perfectly sterilised by dry heat, it must be exposed for half-an-hour at least to a temperature of 160° to 180°. In the experiments of Frosch some species were found capable of multiplication after exposure to the temperature of −87°.

Light has been proved to have an injurious effect upon bacteria. Buchner observed that the vibrio of Asiatic cholera ceased to grow after one hour's exposure to direct sunlight. Hence specialists conclude that free access of light is an important hygienic factor.

Some bacteria have been found by Freudenreich and Serotinin to have an antagonistic action upon the growth of other species. Thus *Bacillus pyogenes fœtidus* prevents the growth of *Spirillum choleræ Asiaticæ.*

The bacteria of putrefaction exert in soils a most important oxidising action. Hence a soil must not be overloaded with organic matter. "The failure of the process of oxidation is well seen in a sewage farm where sewage matter has been applied too freely. Instead of large crops being obtained the reverse is found to be the case, and the land is said to be 'sewage sick.'"

In a series of chapters the authors show the part played by micro-organisms in various diseases.

Foremost comes tuberculosis, which is fully admitted to be infectious and propagated by a special *Bacillus.* It is more prevalent in cold and temperate climates than within the tropics. Milk and meat from tuberculous cows is very infective, and in the ordinary method of cooking the bacillus is not destroyed in the centre of a joint of meat of over six pounds in weight. The virulence of the bacillus is not destroyed by desiccation and preservation as a dry powder for five months. The bacillus has on *post mortem* examination been detected in 40 to 60 per cent of persons who during life had shown no symptoms of the disease. A variety of diseases are here mentioned as inducing a predisposition to phthisis.

It is here mentioned that the Jews enjoy a partial immunity from tubercular disease, and the question is raised whether this may not be possibly due to their care in avoiding diseased meat. It is very judiciously recommended that "health resorts" which are much frequented by consumptive patients should be avoided.

Leprosy is not considered to be hereditary, nor to be influenced by the use of any particular article of food, nor by climate. *E.g.*, it is still endemic in Iceland, South Africa, and the West Indies.

Concerning typhoid fever—a disease fairly evenly distributed over the world—we are warned that carbon filters have been found to be contaminated with the bacillus of this affection. It may also multiply indefinitely in pure water. Milk appears to be another vehicle for the conveyance of the disease. Hence the addition of water—often impure—to milk should be treated as a very serious offence. We have seen the addition to milk of water from a very impure road-side ditch. Dust storms in India, South Africa, and some parts of Australia is another medium for conveyance.

The transmission of malarial disease by a microbion seems to be recognised, mosquitoes and gnats effecting the inoculation. In some persons the irritation due to a gnat bite subsides and reappears after the lapse of a certain time. The remarks on diphtheria will be found well worthy of a careful perusal. Space does not allow us to extend our examination beyond pointing out that the authors clearly recognise the mischief occasioned by the repeal of the so-called "C. D." Acts.

We think this book deserves to be studied not merely by professional men, but by the members of County Councils and all persons having to concern themselves with public health.

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*Chemistry for Beginners.* By EDWARD HART, Ph.D., Professor of Chemistry, Lafayette College, Eastern Pennsylvania, Ex-Fellow Johns Hopkins University, Editor of the *Journal of the American Chemical Society.* Third Edition, revised and greatly enlarged. Eastern Pennsylvania: Chemical Publishing Co. 1896. Pp. 245.

WE have here a very fair specimen of a class of work which has been of late not merely abundant, but even occurring in excess. Dr. Hart's book, unlike many of its class, embraces not merely the inorganic, but also the organic compounds. The nomenclature adopted is somewhat peculiar, the names of the four halogens, F, Cl, Br, and I, are written without the final e customary on the eastern side of the Atlantic, and their compounds are curtailed in a corresponding manner, thus fluorid, chlorid, &c. We submit that the retrenchment might be usefully carried a stage further as far as the halogens are concerned, so as to write fluor, chlor, brom, &c. This would not only bring us into harmony with Continental usage, but would be found more convenient in the formation of compound terms. The final *us* in phosphorus might also be advantageously eliminated.

Some statements in this book seem little adapted for the British, or, indeed, for the European reader. Thus, there is no mention of tellurium as a product of Transylvania. The account of basic slag contains no reference to the discovery by Thomas and Gilchrist.

We doubt whether the quantity of copperas made as a by-product in the manufacture of steel and iron wire exceeds or even equals that obtained by exposing layers of ferrous sulphide to air and rain and concentrating the lixivium and allowing it to crystallise.

Rich deposits of tin-stone are now worked in Tasmania.

It may be asked whether the portion of this work treating of organic chemistry might have been rendered fuller and more instructive if less space had been devoted to graphic formulæ. As it is the organic bases receive but a scanty notice. It is certainly true that vanillin is now made artificially from the inner bark of pine trees, but the natural product is still able to hold its own.

Caoutchouc is not peculiar to the sap of *Siphonia elastica,* but is found also in that of *Ficus elasticus* (India) and *Hovea elastica* (Tropical Africa). Not improbably a fourth rubber-yielding tree will be found in New Guinea or the tropical regions of Australia.

Tannin is a substance, or rather a group of substances, very imperfectly known.

The cautions found *passim* in this book concerning explosives and poisons are very judicious. Prof. Hart may, perhaps, be considered to have written from a too exclusively American point of view; but among medium-sized text-books we should certainly give his work the preference to a vast number of others.

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*Everybody's Medical Guide.* A Handbook of reliable Medical Information and Advice. By M.D. (Lond.). London: Saxon and Co. Pp. 122.

THIS little and handy book is, as we are candidly told in the preface, not designed to supersede the physician, whose advice is always to be preferred. Quack medicines and their accompanying pamphlets generally disappoint the purchaser because they fail in the capital point of diagnosis. It is here remarked that "one of the causes why Englishmen suffer so frequently from constipation is that they have such unbounded faith in advertised pills." It is amusing to read that Professor X Y's pills must be perfectly harmless as they are purely vegetable. The ignorance which can permit a compounder of medicines to pen such a sentence appears almost criminal if we

remember that no mineral is nearly as poisonous as the vegetables belladonna, foxglove, hemlock, nux vomica, &c. Among the possible causes of diarrhœa we find no mention of brown bread. To persons having a tendency to constipation such breads may be beneficial; but in others the particles of bran, however finely ground, produce an iritation which leads to chronic diarrhœa.

We find that not a few "proprietary articles" are here recommended, such as zymine, Kepler solution of cod-liver oil, hazeline, Wyeth beef-juice, &c. We are glad to find it here laid down that the use of "antipyrine" is not without danger.

This book may be safely recommended, especially to persons residing in remote country districts.

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*A Guide to Practical Chemistry for the Conjoint Board.* By PERCY A. E. RICHARDS, F.I.C., F.C.S. London: Baillière, Tindall, and Cox. 8vo., pp. 57.

FORTUNATELY this little book is provided with a rather more explicit title, or we might suppose that the author was guilty of satirising the Conjoint Board. The second title runs "Guide to the Examinations in Practical Chemistry for the Conjoint Board," thus showing that the modicum of chemical lore herein contained was destined for the examinees but not for the Board itself. In all sober sadness we must ask whether such a book can have any *locus standi?*

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# CORRESPONDENCE.

## ARGON AND HELIUM.

### *To the Editor of the Chemical News.*

SIR,—I observe on p. 180 of the present volume of the CHEMICAL NEWS a statement by Herr Siegfried Friedländer to the following effect.

"Crookes has hitherto pointed to the possibility of the compound nature of argon, in reliance upon spectroscopic investigation. J. M. Eder and E. Valenta consider this view as not excluded. But whilst the last mentioned investigators have examined only the red spectrum of argon, Crookes has observed both spectra, of which the red one is best visible at a pressure of 3 m.m., and at a reduced pressure changes into blue. Crookes has shown that it is not easy to obtain the blue spectrum quite free from the red, whilst in some circumstances the red spectrum does not change into the blue. Armstrong, indeed, thought that this need not be recognised as an evidence of the composite character of argon, since also nitrogen, hydrogen, and oxygen display such spectra. But as hitherto in these elements both spectra have never been seen simultaneously, Armstrong's view need not be accepted as a strict proof of the elementary nature of argon. I myself regard the phenomenon observed, that both the spectra of argon appear simultaneously, as one of the weightiest proofs that Lord Rayleigh and Prof. W. Ramsay have revealed two new elements by their discovery of argon."—*Zeitschrift für Physikalische Chemie,* xix., p. 657, and CHEMICAL NEWS, lxiv., p. 180, 1896.

The statement that both spectra of hydrogen, nitrogen, and oxygen have never been seen simultaneously is, I believe, contrary to fact. In the case of nitrogen it certainly is, because I have photographs in my possession taken in the year 1879 which show the two spectra of nitrogen obtained simultaneously from the one spark discharge in air, and not in a vacuum tube.

A reference to the *Proceedings of the Royal Society,* lvii., p. 293, Jan. 31, 1895—"The Spectrum of Argon as it appears in the Spark-Spectrum of Air,"—will show that the concluding sentences of my paper are in the following words:—

"I do not attribute much importance to the fact that argon gives two spectra; the red appears to be the spectrum of the first order, or the spectrum of the lower temperature which corresponds thereto; the blue is the line spectrum, or spectrum at the higher temperature. I have photographed simultaneously from the same spark the two spectra of nitrogen as rendered by atmospheric air. It is therefore more likely that argon is one substance and not two. Whether it is a compound or an element is a question into which the following considerations may enter. There are at present no gaseous substances known which can withstand the temperature of the condensed spark without exhibiting the spectra of one or other of the elements of which it is composed. If, therefore, argon were $N_3$ it would disclose the spectrum of nitrogen. As the spectrum is not that of any known substance, it follows that, if a compound, it is a compound of a new element."

I have elsewhere shown how band spectra passed into line spectra (*Phil. Trans.,* clxxxv., pp. 161-212, 1894), and are related to each other, and it is easy to account for the two argon spectra being spectra of one substance.

I merely wish to point out that a serious error appears to have been made in a statement which has received a wide publication and which is not contained in the original literature on the subject.—I am, &c.,
W. N. HARTLEY.

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 14, October 5, 1896.

**Explosive Properties of Acetylene.**—MM. Berthelot and Vieille.—The authors have considered it useful and necessary to define more completely, from a theoretical point of view, and by precise experiments, the explosive character of acetylene, and to signalise, from a practical point of view, what accidents may be produced in the conditions of its use. We must add that these inconveniences do not seem to counterbalance the advantages presented by this illuminant, or to limit its use. It is easy, in fact, to avoid these risks by suitable arrangements. Such as, on the one part, the operator avoids a too sudden escape of the compressed gas, and, on the other hand, takes care to absorb the heat produced by the compressions and internal reactions of the apparatus so as to prevent any notable rise of temperature.

**Correction to a Paper on the Homogeneity of Argon and Helium.**—Prof. W. Ramsay and J. N. Collie. —In a paper laid before the Academy on July 27th we committed an error which we must rectify. We had supposed that when a mixture of the two gases was submitted to diffusion we did not succeed in obtaining both in a state of purity, but that there always remained a mixture of the two gases in certain proportions, according to their densities. It is true that if we take a mixture of 1 part of hydrogen and 4 parts of oxygen the two gases pass through the permeable walls, so that equal quantities of both gases pass in the same time. This fact does not hinder their separation by means of diffusion. The densities calculated for the various fractions of helium are not those which we mentioned. On the contrary, the density of the heavier gas must be 2·133, and that of the lighter 1·874. The fact remains that we have succeeded in separating helium into two parts.

On Beans.—M. Balland.—The bean, especially after decortication, is one of the most nitrogenous foods. The nitrogenous matter in the bean reaches 22·95 per ecnt.

# THE CHEMICAL NEWS.

## ON "TWIN-ELEMENTS."*

### By RICHARD LORENZ.

I APPLY the name "twin-elements" to simple bodies whose atomic weights approach each other very closely in magnitude. The properties of such elements display manifold mutual relations. As the type of such twins we may regard cobalt and nickel. Their atomic weights are nearly equal, their chemical behaviour and occurrence show great similarity, and their separation presents difficulties. But whilst this couple has often been viewed as intimately connected, the fact has been overlooked that other elements bear, as we are about to show, a similar relation.

Of all the elements known to us a great number form such twin pairs in a very striking manner. In order to find such twin elements, let us suppose all the elements arranged according to the magnitude of their atomic weights. We consider the differences between such successive pairs. It appears that this difference is not greater than 1·4 units, in most cases smaller than 1.

The twin elements appear at once if we plot out the elements on a right line according to their atomic weights in such a manner that those with even atomic weights lie on one side of the line and those with odd atomic weights lie on the other side. For this purpose we must round off the atomic weights. In this manner we arrive at the accompanying table, referring the atomic weight of the elements to O = 16. The rounding off of the elements has been adopted only to facilitate a general view, and is by no means required to establish the regularities under consideration. In every case an odd and an even number form a twin group.

We find first boron and carbon. Taking O = 16, find the atomic weight of carbon = 12·003, and that of boron 11·0. The difference of both is 1·003. The two elements therefore are twins. It scarcely requires mentioning that here there exist manifold similarities. Both elements rank among the least fusible known. They both assume the amorphous, graphitoid, and diamond-like state, and in the latter they crystallise together, forming the boron diamond. Both of them do not conform to the law of Dulong and Petit. Sodium and magnesium form a twin pair. Mg = 24·38, Na = 23·058; difference = 1·322. These elements also display manifold similarities. The two following elements, aluminium and silicon, are twins. Their atomic weights are 28·40 and 27·08; difference 1·32. Sulphur and phosphorus also are twins. S = 32·063, P = 31·03; difference 1·633. In a chemical respect the two elements are readily comparable. Potassium and calcium are twins; their atomic weights are 40 and 39·136. Their joint occurrence and many of their relations are chemically manifest. Further twin pairs are chromium and vanadium, with atomic weights 52·15 and 51·21; difference 0·94. Also manganese and iron, with the atomic weights 56·0 and 55·09; the difference 0·91. There is no chemical objection to their juxtaposition. The twin pair cobalt and nickel has been already mentioned. Selenium and bromine have the atomic weights 79·67 and 79·963; difference 0·293. As regards this chemical behaviour they may be well compared with the twin pair S, P. This pair is again formed of two non-metals. The following pair is silver and palladium, with the atomic weights 107·938 and 106·7; difference 1·238. Antimony and tin are also twins; the atomic weight of

* *Zeit. Anorganische Chemie.*

tin, according to the trustworthy determinations of Classen (O = 16), is 119·1, and that of antimony 120·29; difference 1·19, being therefore twins. Both are "semi-metals," and are especially characterised by the behaviour of their sulphides, in consequence of which they follow each other analytically. Tellurium and iodine vary the successive order of their position, in consequence of different determinations of their atomic weights, as is the case with cobalt and nickel. If we take tellurium = 127·6 (Staudenmeier), or in round numbers 128, the difference of their atomic weights (as the atomic weight of I = 126 864) is 0·736 to 1·136; in any case these elements are twins. Chemically they have many similarities. Both are heavy non-metals, and behave to each other like bromine and selenium, or sulphur and phosphorus. The next twins are tungsten and tantalum; atomic weights 184·0 and 182·8; difference 1·2. Lead and bismuth are twin elements, with the atomic weights 208·01 and 206·911, and the difference 1·099.

Hence we have succeeded in finding fourteen pairs, therefore twenty-eight elements which may be regarded as twins:—

|   |          | Atomic weight. | Difference. |
|---|----------|---------------|-------------|
| 1. | Boron        | 11·0    | 1·009 |
|    | Carbon       | 12·003  |       |
| 2. | Sodium       | 20·058  | 1·322 |
|    | Magnesium    | 24·38   |       |
| 3. | Alumininm    | 27·08   | 1·32  |
|    | Silicon      | 28·40   |       |
| 4. | Phosphorus   | 31·03   | 1·033 |
|    | Sulphur      | 32·063  |       |
| 5. | Potassium    | 39·136  | 0·864 |
|    | Calcium      | 40      |       |
| 6. | Vanadium     | 51·21   | 0·94  |
|    | Chromium     | 52·15   |       |
| 7. | Manganese    | 55·09   | 0·91  |
|    | Iron         | 56·0    |       |
| 8. | Nickel       | 58·71   | 0·66  |
|    | Cobalt       | 59·37   |       |
| 9. | Selenium     | 79·07   | 0·893 |
|    | Bromine      | 79·963  |       |
| 10. | Palladium   | 106 7   | 1·238 |
|    | Silver       | 107·938 |       |
| 11. | Tin         | 119·1   | 1·19  |
|    | Antimony     | 120·29  |       |
| 12. | Iodine      | 126·864 | 0·736 |
|    | Tellurium    | 127·6   |       |
| 13. | Tantalum    | 182·8   | 1·2   |
|    | Tungsten     | 184·0   |       |
| 14. | Lead        | 206·94  | 1·099 |
|    | Bismuth      | 208·01  |       |

We may therefore enounce the proposition:—A great number of elements have atomic weights which approach each other very close in pairs, and differ from each other by at most 1·4 units; the proportions of these elements have manifold relations.

### The Distribution of the Twin-Elements over the Series of Atomic Weights.

If we consider the position of the twin-elements over the series of numbers, we see that a great part of them follow each other in immediate succession. Thus, *e.g.*, there follow upon [Na, Mg] [Al, Si], and [P, S]. There then succeed each other [V, Cr], [Mn, Fe], and [Ni, Co]. The twins just named are so distributed that both their even-numbered and their odd-numbered elements differ from each other by the round number 4. Thus we have—

|          | Difference. | |          | Difference. |
|----------|-------------|-|----------|-------------|
| Na 23·058 | 4·022 |   | Mg 24·38 | 4·02  |
| Al 27·08  |       |   | Si 28·40 |       |
| P 31·0    | 3·95  |   | S 32·063 | 3·663 |

Further—

| | Difference. | | | Difference. |
|---|---|---|---|---|
| V 51·21 | } 3·88 | | Ca 52·15 | } 3·85 |
| Mn 55·09 | | | Fe 56·0 | |

If we now extrapolate the system of twins found here over the entire series of atomic weights,—*i.e.*, if we assume that each pair of twins differs from the foregoing pair in round numbers by the atomic weight 4 or multiple of 4, we arrive at the surprising result that all the fourteen pairs of twins hitherto found fit into this scheme.

The atomic weights (in round numbers) of their elements differ always from each other by 4 or a multiple of 4.

The laterally adjacent elements of the above table are twin elements, (*e.g.*, B, C, or Mn, Fe) ; those which stand beneath each other are arranged according to the magnitude of their atomic weight.

### *The Distribution in the Series of Numbers of those Elements which do not form Twins.*

In the foregoing chapter we have seen that if we extrapolate over the entire series of numbers the scheme according to which some successive twins succeed each other, we arrive at all the other twin-elements, but there is a further consequence.

The single elements situate between the pairs of twins are found in the places required by the twin rule. This holds good for almost all the known elements, and it is particularly to be noted that it holds good most decidedly where the atomic weights are most certainly known, and does not hold good (with few exceptions) where the atomic weights are less accurately known.

Thus, *e.g.*, phosphorus and sulphur are a twin pair [31, 32]. The following twin pair should have in round numbers the atomic weights [35, 36], and the next [39, 40]. The last is, in fact, formed by the elements potassium and calcium, but the intermediate space is unoccupied. But between sulphur and potassium lies chlorine, with the atomic weight 35·453, exactly in the middle of the twin pair [35, 36]. In like manner we find copper, arsenic, strontium, molybdenum, &c., in the places of twins.

(To be continued).

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## ON NEW SALTS OF COBALT AND NICKEL.
### (A PRELIMINARY COMMUNICATION.)

#### By NAGENDRA CH. NÂG.

WHILST examining different specimens of bromine in March last, I remarked on a peculiar green colouration in the solution of a cobalt salt. In one experiment bromine with potassium carbonate was added to the solution of cobalt chloride in the expectation of the formation of a hypobromite. But there was formed a green solution like that of a nickel salt. This green solution of a cobalt salt was so striking a fact that I showed it to Professors Pedler and Râly, and they were not acquainted with any cobalt compound of this colour. They advised me, therefore, to undertake experiments for its isolation.

In order to obtain this compound free from potassium chloride, we precipitate cobalt carbonate with an excess of potassium bicarbonate and add bromine. There ensues a strong liberation of carbonic acid, whilst the cobalt carbonate slowly dissolves with a green colour. That this new compound is no bromine combination appears from the fact that it is precipitated along with the excess of bicarbonate on shaking the concentrated solution with alcohol and ether. The filtrate contains all the bromine as a bromide, and may be separated from the new compound by decantation. It is, however, very unstable after precipitation, even in an aqueous solution,

which is probably due to the presence of alcohol. Pressing between filter paper was also not of much use, and all attempts at isolating the new substance proved unsuccessful.

The compound seems to be an oxidation product, perhaps corresponding to the ferrates. If we allow the solution of the compound precipitated by alcohol and ether to stand for some time it is reduced, and displays dichroism, probably due to the presence of a violet-coloured precipitate. If we add to the green solution yellow ammonium sulphide or hydrogen sulphide, there is formed first a deep brown solution, which probably contains a lower oxidation product. It is then further reduced, and there appears a deposit. Ammonia alone likewise reduces it, and the green colour is changed with a probable production of cobalt ammonium compounds.

Experiments to obtain a corresponding nickel compound were unsuccessful. This fact is in accordance with the theory of Mendeleeff, according to which nickel is more electropositive than cobalt.

If instead of treating cobalt carbonate with potassium bicarbonate and bromine we add sodium acetate with bromine, there is formed a dark brown solution. The same experiment gives with salts of nickel a solution similar in colour to potassium bichromate. On boiling the solution of the nickel salt a part of the solution falls as a violet precipitate, and there remains a neutral liquid of an apple-green colour. In such circumstances the salts of cobalt give no precipitate. These, as above suggested, seem to be lower oxidation products, for if we add to the brown solution of a cobalt salt containing bromine in excess potassium bicarbonate, the green solution reappears. That in the case of nickel only the lower products of oxidation appear, and that even these are decomposed on boiling, is explained by the more basic character of nickel. The formation of the salts may perhaps be explained by the following formulæ—

I. $CoCO_3 + 2Br_2 + 6KHCO_3 =$
$$= K_2CoO_4 + 7CO_2 + 4KBr + H_2O.$$

II. *a.* $6NiCO_3 + 2CH_3COONa + 3Br_2 = Na_2Ni_2O_6 + (CH_3COO)_2Ni + 6O_2 + 2Ni + 6CO_2 + 3NiBr_2.$

*b.* $Na_2Ni_2C6 + (CH_3COO)_2Ni = 2CH_3COONa.$
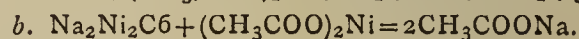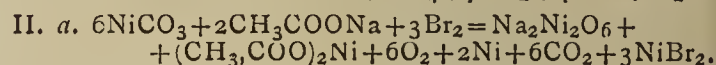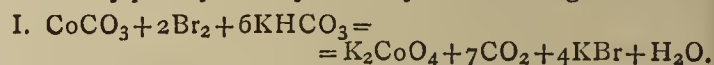
—*Zeitschrift für Anorganische Chemie.*

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## LUCIUM: A NEW ELEMENT, PATENTED!

DRAFT COMPLETE SPECIFICATION OF PROSPER BARRIÈRE, OF PARIS, IN THE REPUBLIC OF FRANCE, FOR IMPROVEMENTS IN THE PREPARATION AND PRODUCTION OF BODIES FOR USE IN WHAT IS KNOWN AS INCANDESCENT GAS LIGHTING.

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INCANDESCENT gas lighting, which consists in suspending fire-proof luminous substances within the flame of a Bunsen burner, has been carried out hitherto in several different ways.

The illuminating properties possessed by various metallic oxides, such as those of the zirconium, lanthanum, yttrium, thorium, and magnesium, have suggested the idea of making these oxides serviceable as luminous bodies.

The distinctive features of the various metallic oxides hitherto employed have been precisely determined from the points of view of both physical science and chemistry.

These oxides are derived from corresponding ores, such as thorite, cerite, gadolinite, zircons, and the like.

The treatment of these ores is a question which has not as yet been fully cleared up, and I shall not attempt to deal with it, inasmuch as my own efforts have been directed to the study of other minerals.

But the numerous experiments which I have made have enabled me to discover and so satisfy myself of the

presence of a novel illuminating body (I will refer to it under the letter A) in a special ore of a sandy nature, obtainable at different places and known as monazited sand.

This body has properties different from those possessed by the substances used hitherto.

The ore, which possesses a sandy appearance, is really rich river loam found in small ruby-like pebbles.

The following is an example of an analysis made on a sample of this substance :—

| | |
|---|---|
| $(SiO_2)$ Silica.. .. .. .. .. .. .. | 69·7 per cent. |
| $(P_2O_5)$ Phosphoric acid .. .. .. .. .. | 6 ,, |
| $(Fe_2O_3)$ Iron.. .. .. .. .. .. .. | 1·92 ,, |
| $(Al_2O_3)$ Alumina .. .. .. .. .. .. | 15 ,, |
| Cerium, lanthanum, didymium, about .. | 2·13 ,, |
| Moisture .. .. .. .. .. .. .. | 2·05 ,, |
| Lime, magnesia, and other miscellaneous matter, about .. .. .. .. .. .. | 2 ,, |
| A body .. .. .. .. .. .. .. .. | 1·80 ,, |

This new body, A, enters into the composition of the ores named in the proportion of from 1·5 to 6 per cent, according to the sample dealt with.

### Treatment.

The composition indicated above necessitates special methods of treatment, having for their object to eliminate any harmful substances which the body treated may contain.

The purity of this body is the main condition upon which a satisfactory yield depends.

The ore, on having been porphyrised, is slowly melted in suitable furnaces, with an addition of carbonate of sodium in the proportion of one part of ore for every two parts of carbonate. This operation, which takes about three hours to complete, is intended to convert the oxides into insoluble carbonates.

After cooling, the powdered mass is lixiviated; thus, by means of decantation, the elimination of the silicates and phosphates of sodium is proceeded with.

When the carbonates are exhausted by the water, they are subjected to the action of the sulphuric acid, the surplus of which is eliminated by slow calcination ; the sulphates are dissolved in cold water and precipitated by means of ammonia. The precipitate, on being washed, is dissolved in hydrochloric acid, care being taken to properly neutralise it.

The greater part of the iron and alumina is then removed by precipitating it by means of oxalic acid.

The insoluble oxalates are converted into sulphates, when partial calcination in a muffle-furnace is proceeded with.

This calcination is interrupted at a certain period of the operation, which, however, can only be determined by taking into account the appearance of the material under treatment, the proper time for this being when the greater part of the acid has been eliminated. The sulphates obtained are then pulverised and put in cold water in small quantities, so that the saturation stage is, as nearly as possible, reached.

The solutions obtained is then precipitated by means of ammonia, whereby magnesia and the salts of lime are eliminated. Then, by filtering, a gelatinous precipitate of oxides is obtained, which is dissolved in sulphuric acid.

The sulphuric solution obtained, having had sulphate of sodium in solution, saturated while cold, added to it, is used as a precipitating medium, there being crystals in suspension in the mass, and the saturated solutions being allowed to digest for from five to six hours, thus the group, cerium, lanthanum, didymium, is precipitated.

The double sulphates thus obtained are filtered and then thoroughly washed.

In order to remove thorium, the solution is made in sulphuric acid, and the precipitate obtained by means of sulphate of potassium.

Thus all the bodies mentioned above, as being present with the A body, may be eliminated.

Now the principal operation of the process has to be commenced. It consists in precipitating the solution by means of hyposulphite of sodium in the condition of a concentrated solution. This operation is started with a slight action of heat. When the boiling point is reached, the A body is precipitated first. The body obtained contains as impurities small quantities of ytterite earths, principally ytterbia.

It only remains after this to effect a most thorough washing of the hyposulphite thus obtained, using cold water for the purpose. After the washing a solution is made in hydrochloric acid.

A reaction with sulphocyanide of ammonium will at that moment show whether there are any traces of iron left, and these, if present, may then be eliminated by the ordinary methods.

In the same way, traces of other metallic substances may be eliminated by means of a current of sulphuretted hydrogen sent into the solution of hydrochloric acid.

After precipitation by means of ammonia, the body is energetically washed with distilled cold water.

By such means a body is obtained which in itself is luminous, and which is made use of in the manner which I will now describe.

Generally speaking, the oxides employed for illuminating purposes, as well as the body to which I have referred just now, produce light which is illuminating and radiating only to a certain degree.

Radiation which constitutes the illuminating power proper, and more particularly the brilliancy desirable in a luminous body, is obtained owing to the molecular conditions which I have found to be realisable with exceptional ease in a body which, after many trials, I have discovered to be oxide of zinc. Any other body fulfilling the same conditions may, however, be employed without departing from the principle of the inventions.

Oxide of zinc, which upon being heated at an ordinary temperature assumes a greenish-yellow hue, when subjected to the heat of a Bunsen burner, becomes phosphorescent as it were. It is sufficient to add a small percentage of it to the illuminating solution.

I employ a nitric solution of the oxide in question.

After a fabric, which should be as fibrous as possible, has been impregnated with the said solution, when the wick thus formed has been incinerated, the decomposition of the nitrates will take place under the most favourable conditions conceivable.

Part of the oxide of zinc, the surplus thereof, is volatilised, while the remainder will be in that molecular condition referred to just now.

It is not impossible to use other oxides which, if employed under certain conditions, and mixed or combined in a certain definite manner, and either combined or not with the body A, may form novel bodies.

The fabric which I employ is made of special thread or filament, such as the fibres of flax, china grass, or the like, and it should have about 90 meshes per square centimetre. It is washed in a one-tenth solution of hydrochloric acid, and then with water having a slight amount of ammonia incorporated in it.

The fabric after drying is cut into strips of say 20 centimetres, and strengthened at their upper part with a strip of muslin or tulle.

Impregnation may be advantageously substituted by aspersion, by means of a special injector, which process offers the advantage of not necessitating protracted handling of the fabric whereby certain impurities might find their way into it.

The bath employed is a nitric aqueous solution, containing as much as 10 per cent of the luminous body. Each wick should absorb at least 6 cubic centimetres.

After the wick has been placed on a special form of mould, it is secured to a hanger of nickel by means of an asbestos thread.

A Bunsen flame is rapidly and circularly passed round the upper portion of the said wick, while another burner is worked from below. Incineration will then take place, and the earths will form gradually. By such means a skeleton is obtained, which is placed over a burner for about half-an-hour in order to secure complete calcination; the wick is then in readiness for being supplied in a marketable form, and may be fitted to any burner.

The novel illuminating body, which I have referred to as A, I have named "Lucium."

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is—

1. For incandescent gas lighting a new body derived from monazite sands, substantially as hereinbefore described.

2. For incandescent gas lighting the body A referred to in the preceding claim, in combination with a small percentage of oxide of zinc or other body capable of imparting the necessary intensity and power of radiation as hereinbefore specified.

3. The purification of the A body, referred to in the first claim by treating monazite sands by oxalic acid, sulphate of sodium, sulphate of potassium, and hyposulphite of sodium, substantially as described.

4. For incandescent gas lighting the combination of the aforesaid body A (either alone or in combination with other bodies, as indicated in the second claim) with fibres or filaments substantially as and for the purpose hereinbefore specified.

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## SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.*

### By GEORGE AUCHY.†

VOLHARD's method of determining manganese is generally considered a very accurate one; nevertheless, that the accuracy of the process is strictly dependent upon certain conditions and precautions not pointed out by the author, and not generally recognised (so far as the writer is aware) seems proved by the experience with the method and with Stone's modification of it, which follows :—

### *Stone's Modification.*

Mr. Geo. C. Stone makes a very considerable saving in time by omitting the evaporation with sulphuric acid, and precipitating the iron immediately with zinc oxide as soon as solution of the drillings in nitric acid is effected.‡ But in Volhard's original article, as also in Blair's "Chemical Analysis of Iron," it is directed to destroy the carbonaceous matter by evaporation to dryness and strongly heating, or by evaporation with sulphuric acid till fumes of the latter come off, and as previous to the appearance of Mr. Stone's paper the writer—on testing this point by dissolving in sulphuric acid with enough nitric added to oxidise the iron and help to effect the solution of the drillings and omitting the evaporation — had obtained results several hundredths higher (although Volhard's objection to organic matter is that it hinders the balling together of the manganese dioxide in titration) than those obtained from the same samples by the regular process, it was judged that this precaution was not a useless one; and after reading Mr. Stone's article it was therefore con-

sidered well, as a precaution, to test his process also in this particular, and for that purpose the following determinations were made :—

TABLE I.

| No. | Carbon. | Volhard's method. | Stone's modification. |
|---|---|---|---|
| | Per cent. | Per cent. | Per cent. |
| 476 | 0·585 | 0·46 | 0·53 |
| 495 | 0·80 | 0·57 | 0·65 |
| 503 | 0·228 | 0·423 | 0·45 |
| 505 | 0·225 | 0·49 | 0·52 |
| 483 | 0·17 | 0·43 | 0·51 |
| 486 | 0·185 | 0·54 | 0·61 |
| 507 | 0·315 | 0·44 | 0·44 |

The results of Stone's method were very considerably higher than those by the regular method, except in the case of 507. But in the case of 507 it was noted that in making the precipitation of the iron by the zinc oxide a large excess had been accidentally used, while in all the other determinations the zinc oxide had been added in amount sufficient to precipitate the iron merely; and it was therefore thought advisable to see whether the considerable differences in the results by the two methods— Volhard's and Stone's—was not due to this fact (insufficient neutralisation in the latter) before attributing it to the organic matter undestroyed in Stone's method. The above determinations were therefore repeated, using in each case not only enough zinc oxide to coagulate the solution and precipitate the iron as directed, but also enough in excess of this amount to turn the brownish red colour of the iron precipitate to a light brown. The results follow :—

TABLE II.

| No. | Carbon. | Volhard. | Stone. Zinc oxide to coagulation. | Stone. Zinc oxide in large excess. |
|---|---|---|---|---|
| | Per cent. | Per cent. | Per cent. | Per cent. |
| 503 | 0·228 | 0·423 | 0·45 | 0·45 |
| 505 | 0·225 | 0·49 | 0·52 | 0·51 |
| 483 | 0·17 | 0·43 | 0·51 | 0·45 |
| 483 | 0·17 | 0·43 | 0·51 | 0·45 |
| 486 | 0·185 | 0·55 | 0·61 | 0·58 |
| 486 | 0·185 | 0·54 | 0·61 | 0·58 |
| 476 | 0·585 | 0·46 | 0·53 | 0·47 |
| 495 | 0·80 | 0·57 | 0·65 | 0·60 |
| 471 | 0·105 | 0·38 | — | 0·40 |
| 480 | 0·10 | 0·35 | — | 0·36 |
| 493 | 0·57 | 0·46 | — | 0·47 |
| 507 | 0·315 | 0·435 | — | 0·44 |
| 153 | 0·50 | 0·64 | — | 0·70 |
| 153 | 0·50 | 0·64 | — | 0·67 |
| 153 | 0·50 | 0·64 | — | 0·69 |
| 155 | 0·40 | 0·56 | — | 0·56 |

These results show that when the zinc oxide is added merely to coagulation and precipitation of the iron, leaving the solution probably faintly acid, the manganese is afterward precipitated, not according to the theoretical formula, but with result too high; and that to insure the correct precipitation of the manganese it is necessary to add the zinc oxide in large excess, so that the solution is thoroughly neutralised when titrated.

It will, however, be noted that with this precaution, observed results in this table are nevertheless a few hundredths per cent higher than by Volhard's method.* Is this difference due to the undestroyed carbonaceous matter? It was thought probable, but, to make sure, some of the tests were repeated with oxidation of the

carbonaceous matter by addition of lead dioxide to the boiling nitric acid solution of the drillings (the excess destroyed by ferrous sulphate and the excess of the latter oxidised by continued boiling of the nitric acid solution).* These results should be lower if carbonaceous matter has any influence. They were not lower, as the following table shows, and hence it is indicated that carbonaceous matter does not interfere. It is true that in one case (483) the result obtained by oxidation of the carbonaceous matter is lower, but the reason for this will appear later on.

TABLE III.

| No. | Carbon. Per cent. | Stone. With carbon not oxidised. Per cent. | Stone. With carbon oxidised. Per cent. |
|---|---|---|---|
| 480 | 0·10 | 0·36 | 0·37 |
| 507 | 0·315 | 0·44 | 0·44 |
| 155 | 0·40 | 0·56 | 0·55 |
| 155 | 0·40 | 0·56 | 0·57 |
| 155 | 0·40 | 0·56 | 0·56 |
| 155 | 0·40 | 0·56 | 0·56 |
| 153 | 0·50 | 0·70 | 0·68 |
| 483 | 0·17 | 0·45 | 0·41 |

Since the slightly high results obtained by Stone's method, in Table II., are not due to the undestroyed carbonaceous matter, they must be due to the fact of titration in nitric acid solution. The following determinations of manganese in solutions containing no organic matter, and in which the amount of manganese was known (made by taking definite amounts of standard permanganate solution) are confirmatory of this conclusion :—

TABLE IV.

| No. | Manganese taken. Per cent. | Manganese found. Per cent. |
|---|---|---|
| 1. | 0·40 | 0·41 |
| 2. | 0·40 | 0·41 |
| 3. | 0·40 | 0·41 |
| 4. | 0·40 | 0·41 |
| 5. | 0·40 | 0·41 |
| 6. | 0·40 | 0·41 |
| 7. | 0·40 | 0·42 |
| 8. | 0·40 | 0·42 |
| 9. | 0·80 | 0·81 |
| 10. | 0·80 | 0·82 |
| 11. | 1·20 | 1·24 |
| 12. | 1·20 | 1·22 |
| 13. | 0·80 | 0·81 |
| 14. | 1·20 | 1·22 |

Here, then, is a second precaution to be observed in Stone's method : a correction of the result by one or two hundredths per cent must in each case be made. But still other precautions are necessary, as will appear.

(To be continued).

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# ON THE INVERSION OF SUGAR BY SALTS.†
## No. II.

By J. H. LONG.
(Continued from p. 204).

*Potassium Alum.*

SOLUTIONS of this salt invert very rapidly. A sample of pure alum was crystallised several times from distilled water to secure a product free from traces of uncombined sulphuric acid, sometimes present in the commercial article. This carefully purified salt was used in all the inversion tests. In the tables below, $t$ refers to the time in minutes, and

*Experiment 1.*
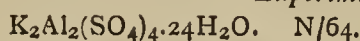
$K_2Al_2(SO_4)_4.24H_2O.$   N/64.
In 250 c.c., 50 grms. of sugar + 0·617 grm. of alum.
A = 33·03°.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 24·73° | — | — | — |
| 15 | 20·15 | 4·58° | 0·06483 | 0·00432 |
| 30 | 16·16 | 8·57 | 0·13045 | 0·00434 |
| 60 | 9·75 | 14·98 | 0·26243 | 0·00437 |
| 90 | 4·85 | 19·88 | 0·39998 | 0·00444 |
| 120 | 1·25 | 23·48 | 0·53891 | 0·00449 |
| 150 | −1·30 | 26·03 | 0·67581 | 0·00449 |
| 210 | −4·88 | 29·61 | 0·98488 | 0·00468 |
| 270 | −6·40 | 31·13 | 1·24016 | 0·00459 |
|  |  |  |  | 0·00446 |

*Experiment 2.*
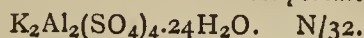
$K_2Al_2(SO_4)_4.24H_2O.$   N/32.
In 250 c.c., 50 grms of sugar + 1·234 grms. of alum.
A = 32·37.

| 0 | 24·07° | — | — | — |
|---|---|---|---|---|
| 15 | 17·83 | 6·24° | 0·09300 | 0·00620 |
| 30 | 12·92 | 11·15 | 0·18339 | 0·00611 |
| 60 | 5·50 | 18·57 | 0·37026 | 0·00612 |
| 90 | 0·75 | 23·32 | 0·55349 | 0·00615 |
| 120 | −2·48 | 26·55 | 0·74522 | 0·00621 |
| 150 | −4·76 | 28·83 | 0·96114 | 0·00641 |
| 210 | −7·00 | 31·07 | 1·39620 | 0·00661 |
| 270 | −7·80 | 31·87 | 1·81117 | 0·00670 |
|  |  |  |  | 0·00632 |

*Experiment 3.*
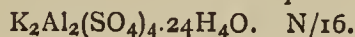
$K_2Al_2(SO_4)_4.24H_4O.$   N/16.
In 250 c.c., 50 grms. of sugar + 2·468 grms. of alum.
A = 31·25.

| 0 | 22·95° | — | — | — |
|---|---|---|---|---|
| 15 | 14·80 | 8·15° | 0·13124 | 0·00875 |
| 30 | 8·79 | 14·16 | 0·26211 | 0·00873 |
| 60 | 1·07 | 21·88 | 0·52311 | 0·00872 |
| 90 | −3·03 | 25·98 | 0·77304 | 0·00859 |
| 120 | −5·64 | 28·59 | 1·06997 | 0·00891 |
| 180 | −7·53 | 30·48 | 1·55533 | 0·00864 |
| 240 | −8·15 | 31·10 | 2·31866 | 0·00966 |
|  |  |  |  | 0·00886 |

*Experiment 4.*
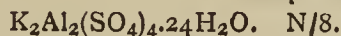
$K_2Al_2(SO_4)_4.24H_2O.$   N/8.
In 250 c.c., 50 grms. of sugar + 4·936 grms. of alum.
A = 30·03.

| 0 | 21·73° | — | — | — |
|---|---|---|---|---|
| 15 | 11·23 | 10·50° | 0·18686 | 0·01245 |
| 30 | 4·45 | 17·28 | 0·37205 | 0·01240 |
| 60 | −2·87 | 24·60 | 0·74276 | 0·01238 |
| 90 | −5·95 | 27·68 | 1·10649 | 0·01230 |
| 120 | −7·34 | 29·07 | 1·49529 | 0·01244 |
| 180 | −8·18 | 29·91 | 2·39838 | 0·01332 |
|  |  |  |  | 0·01255 |

*Experiment 5.*
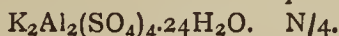
$K_2Al_2(SO_4)_4.24H_2O.$   N/4.
In 250 c.c., 50 grms. of sugar + 9·872 grms. of alum.
A = 29·19.

| 0 | 20·89° | — | — | — |
|---|---|---|---|---|
| 10 | 10·89 | 10·00° | 0·18216 | 0·01822 |
| 25 | 2·10 | 18·79 | 0·44820 | 0·01793 |
| 50 | −4·70 | 25·59 | 0·90893 | 0·01818 |
| 90 | −7·73 | 28·62 | 1·70936 | 0·01899 |
| 150 | −8·25 | 29·14 | 2·76626 | 0·01844 |
|  |  |  |  | 0·01835 |

under $a$ is given the observed angle of rotation in degrees and hundredths.

An attempt was made to invert with a half normal solution, but at the temperature employed the rate was found to be too rapid for accurate observation.

With the first four solutions no difficulty was found in making accurate polarimetric observations in the 200 m.m. tube. The last solution, however, became finally somewhat coloured, and slightly turbid from precipitation of what appeared to be aluminum hydroxide. A portion heated 180 minutes became too turbid for direct reading, and had to be examined in the 100 m.m. tube after filtration. The rotation was found now to be $-3\cdot60°$, corresponding to $-7\cdot20°$ for the 200 m.m. tube, instead of $-8\cdot25$ or $-8\cdot30°$. From the slight concentration due to the filtration a still greater negative value instead of a lower one should be expected. We have here an illustration of the fact referred to above, viz., that prolonged heating makes the end-point determination somewhat uncertain at times.

It is interesting to note the relation existing between the concentrations of the solutions and their rates of inversion in the above examples. For comparison, we call the lowest concentration unity and arrange them as follows :—

| Conc. | | K. |
|---|---|---|
| N/64 | 1 | 0·00446 |
| N/32 | 2 | 0·00632 |
| N/16 | 4 | 0·00886 |
| N/8 | 8 | 0·01255 |
| N/4 | 16 | 0·01835 |

Inspection of the table shows that the coefficient, K, increases rapidly with the concentration, but is not directly proportional to it. It is apparent that the numbers in the third column vary approximately as the square roots of those in the second, which is clearly shown in the next table :—

| Conc. | K. | $K_1 \times \sqrt{Conc.}$ |
|---|---|---|
| 1 | 0·00446 | 0·00446 |
| 2 | 0·00632 | 0·00631 |
| 4 | 0·00886 | 0·00892 |
| 8 | 0·01255 | 0·01261 |
| 16 | 0·01835 | 0·01784 |

The regular results obtained from the aluminum salt are probably due in a measure to the inertness of the hydroxide toward sugar, as well as to the behaviour of sulphuric acid in inversion. The bases of the other salts examined below form combinations with sugar more or less readily, not only with saccharose, but also with the products of inversion, so that the normal results of the reaction may be modified in a manner difficult to compute. The rather rapid rate of inversion in the above points to a relatively great degree of hydrolysis in the alum. Walker and Aston (*loc. cit.*) found something similar in a half normal solution of the nitrate, studied at a temperature of 80°. From their polarisations a value of 0·0077 for K was found, and this was much in excess of the values found for other salts at the same time.

*Ferrous Sulphate.*

A sample of the purest obtainable sulphate was re-crystallised from water containing a trace of sulphuric acid, then dissolved in distilled water and precipitated by alcohol. The crystal meal secured was washed several times with alcohol and dried by fanning. The finished product was bright green and gave a nearly clear solution with pure water. It still held a trace of alcohol, as disclosed by the odour. The experimental solutions were made by dissolving the sugar first and adding to this syrup the weighed sulphate meal. The mixtures were shaken to complete solution without application of heat, and then poured into the tubes for inversion. The solutions soon became turbid on warming, and a minute amount of flocculent precipitate separated, making direct polarisation impossible. The readings could be made therefore only after filtration, which was not without slight effect on the result. The total amount of separated hydroxide or basic salt was, and remained through the test, minute.

*Experiment 6.*

$FeSO_4.7H_2O.$   N/2.
In 250 c.c., 50 grms. of sugar $+$ 17·38 grms. of sulphate.
A = 17·12.

| $t.$ | $a.$ | $x.$ | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 12·97 | — | — | — |
| 15 | 12·48 | 0·49 | 0·01261 | 0·00084 |
| 45 | 11·50 | 1·47 | 0·03899 | 0·00086 |
| 75 | 10·40 | 2·57 | 0·07064 | 0·00094 |
| 135 | 8·43 | 4·54 | 0·13382 | 0·00099 |
| 195 | 6·72 | 6·25 | 0·19727 | 0·00101 |
| 255 | 5·21 | 7·76 | 0·26222 | 0·00102 |
| 375 | 2·87 | 10·10 | 0·38716 | 0·00103 |
| 495 | 1·03 | 11·94 | 0·51917 | 0·00105 |
| | | | | 0·00099 |

*Experiment 7.*

$FeSO_4.7H_2O.$   N.
In 250 c.c., 50 grms. of sugar $+$ 34·75 grms. of sulphate.
A = 17·10.

| 0 | 12·95 | — | — | — |
|---|---|---|---|---|
| 15 | 12·45 | 0·50 | 0·01289 | 0·00086 |
| 45 | 11·26 | 1·69 | 0·04520 | 0·00100 |
| 75 | 10·08 | 2·87 | 0·07980 | 0·00106 |
| 135 | 8·07 | 4·88 | 0·14593 | 0·00108 |
| 195 | 6·30 | 6·65 | 0·21388 | 0·00110 |
| 255 | 4·70 | 8·25 | 0·28606 | 0·00112 |
| 375 | 2·25 | 10·70 | 0·42682 | 0·00114 |
| 495 | 0·15 | 12·80 | 0·59953 | 0·00121 |
| | | | | 0·00107 |

Other tests were made with a second preparation of ferrous sulphate from which the alcohol had not been as completely removed. For a half normal solution the coefficient 0·00094 was found, and for a normal solution the value 0·00100; both results being but a trifle lower than those obtained from the pure products. It is possible that the differences may be due to the presence of the trace of alcohol. In any case it is evident that with solutions as strong as those used the larger amount of sulphate inverts but little more rapidly than the smaller.

(To be continued).

## THE APPROACHING JUBILEE OF SCIENCE TEACHING IN THE CITY OF LONDON SCHOOL.

ON Thursday, October 22nd, a preliminary meeting of Old Scholars was held in the library of the City of London School, for the purpose of considering the desirability of taking steps to celebrate the forthcoming Jubilee of Science Teaching at their school. There was a good attendance, and Dr. William Garnett was invited to take the chair. An original prospectus of Mr. Thomas Hall's first course of lectures, bearing date March 12th, 1847, was produced, which announced the determination of the then school committee to introduce the subject of Chemistry, with accompanying syllabus. Two of Mr. Hall's earliest pupils who were present—Messrs. J. C. Harker and J. Spiller —affirmed that they actually attended these lectures in 1847, and it was commonly believed that they constituted the first successful endeavour to introduce the study of natural science into the curriculum of a public school. Having regard to the large number of students who had been thus induced to qualify for entering the scientific professions, and the early date of such technical teaching,

it was thought that the Corporation of the City of London might possibly be inclined to join in the celebration of an event at once so interesting and creditable to the Municipal authorities.

Resolutions were passed, and an influential committee was formed to take steps in the direction indicated. Dr. W. H. Perkin, F.R.S., being elected chairman, Mr. Alexander Mortimer, M.A., treasurer, and Messrs. Henry Durham, F.C.S., and John Spiller, F.C.S., were requested to act as joint-secretaries. It was suggested that a "Hall Memorial Fund" should be raised for the purpose of instituting prizes, or founding a scholarship, for the encouragement of scientific studies. Also that, if possible, a conversazione should be held at some convenient date shortly before Easter, 1897.

## THE SCIENTIFIC DEPARTMENT OF THE IMPERIAL INSTITUTE.

THE extended organisation of the experimental branch of the Scientific and Technical Research Department of the Imperial Institute is now nearly complete, and the whole of the west corridor of the second floor is occupied by well-equipped laboratories, instrument rooms, and sample examination rooms, whilst the recently appointed staff of skilled chemists is already engaged in the scientific and technical investigation of numerous Indian and Colonial products, which are likely to prove of commercial importance or of scientific interest.

The Winter Course of Lectures will be opened on Monday, November 9th, at 8.30 p.m., with a discourse by Professor Wyndham Dunstan, F.R.S., the recently-appointed Director of the Scientific Department, the subject of which will be "Illustrations of some of the Work of the Scientific and Technical Research Department of the Imperial Institute." After the lecture the Research Laboratories of the Department will be open for the inspection of visitors, and a number of interesting exhibits will be on view.

On November 16th Mr. William Crookes, F.R.S., will deliver the first of two illustrated lectures on the "Diamond Mines of Kimberley," in connection with which a number of specimens and experiments of great interest will be shown. Among other topics Mr. Crookes will discuss the nature and probable origin of the diamond, and will give an account of recent researches of his own. On the occasion of the first lecture Lord Loch will preside.

On the two remaining Monday evenings in November illustrated lectures will be given by Prof. J. W. Judd, C.B., F.R.S., the Dean of the Royal College of Science, on "Rubies, Natural and Artificial, with special reference to their Occurrence in the British Empire" (November 23rd), and by Dr. J. H. Bryan, F.R.S., on "Flight, Natural and Artificial" (November 30th).

Succeeding lectures, the dates of which will be duly announced, will be given by Prof. A. H. Church, F.R.S., Professor of Chemistry to the Royal Academy, on "Some Food-grains of India"; by Dr. Schlich, C.I.E., of the Royal Indian Engineering College, Cooper's Hill, on "The Timber Supply of the British Empire"; by the Hon. W. Pember Reeves, Agent-General for New Zealand, on "The Hot Springs District of New Zealand"; by Colonel Watson, R.E., on "Schools of Modern Oriental Study"; by Mr. A. Montefiore Brice, F.R.G.S., on "The Results of the Jackson-Harmsworth Expedition"; A course of three lectures by Dr. J. L. W. Thudichum, F.R.C.P., on "The Nature and Manufacture of Wine, with special reference to Colonial Wines"; by Prof. J. Norman Lockyer, C.B., F.R.S., on "How the British Empire aids in Solar Enquiries"; by Prof. W. E. Ayrton, F.R.S., on "Sixty Years of Submarine Telegraphy"; and by Mr. Spencer Pickering, F.R.S., on "The Woburn Experi-mental Fruit Farm." These lectures are open to Fellows of the Institute, and to persons introduced by them.

## INVESTIGATION TO DETERMINE WHETHER DIPHENYLIODONIUM AND THALLIUM NITRATES ARE ISOMORPHOUS.

By A. A. NOYES. Ph.D., and C. W. HAPGOOD, S.B.

THE great similarity in properties observed by V. Meyer (*Berichte der Deutschen Chemischen Gesells.*, xxvii., 502, 1592) between the salts of thallium and diphenyliodonium, $(C_6H_5)_2I \cdot OH$, made it seem not improbable that they might be also isomorphous with each other. The matter seemed worthy of investigation, as only a few such cases of isomorphous replacement of single atoms by complex organic radicals are known.

According to the extended investigations of Retgers, by far the most reliable criterion of isomorphism is furnished by the power of the substances in question of forming homogeneous mixed crystals with the proportions varying continuously within wide limits. Consequently, the experimental method based on this principle as described by Retgers (*Zeitsch. fur Physikalishe Chemie*, iv., 593) was followed, chemical analysis and specific gravity determinations being employed to determine the character of the crystals separating from the solution. Preliminary experiments showed that the largest and most perfect crystals were obtained with the nitrates when crystallised from alkaline solution. Saturated solutions of thallous nitrate in water and of diphenyliodonium nitrate (made as described by Hartmann and V. Meyer, *Berichte der Deutschen Chemischen Gesellschaft*, xxvii., 506) in a moderately strong aqueous solution of the free base, diphenyl-iodonium hydrate, were therefore prepared, mixed with each other in crystallising dishes in varying proportions, and allowed to stand in a vacuum desiccator till a sufficient quantity of crystals had separated. The solutions were mixed in the following proportions, the number of parts of the diphenyliodonium nitrate solution being given first :—10 : 1·1 ; 10 : 2; 10 : 5; 10 : 6·7; 10 : 10; 10 : 15; 10 : 20; 10 : 50 ; and 10 : 90.

The first crop from the last solutions consisted of two distinct kinds of crystals, one kind much lighter and the other much heavier than methylene iodide. In all the other cases only one kind of crystals, which was lighter than methylene iodide, was obtained. The specific gravity of these lighter crystals separating from each of the nine solutions was determined by the suspension method of Retgers (*Zeits. f. Phys. Chem*, iii., 289), the value taken being that corresponding to the heaviest crystals of each lot. The results varied irregularly between 1·866 and 1·889. For the pure diphenyliodonium nitrate we found 1·868. For thallous nitrate Lamy (*Ann. de Chem. et de Phys.* (3), lxvii., 409) found 5·8. The lighter crystals were therefore in all nine cases practically pure diphenyliodonium nitrate. The heavier crystals from the last solutions were mixed together, dried at 100°, and analysed by heating in a crucible with concentrated sulphuric acid and igniting. Two separate determinations showed them to contain 99·83 and 99·93 per cent of thallous nitrate.

Thus the two salts crystallise out separately from the solution in the pure state, not in the form of mixed crystals. They are therefore not isomorphous.—*Technology Quarterly and Proceedings of the Society of Arts*, ix., p. 236.

Sir Charles Cameron.—On Friday last, 23rd inst., the Royal University of Ireland conferred the degree of M.D., Honoris Causâ, on Sir Charles A. Cameron, ex-President, and Professor of Chemistry and Hygiene, R.C.S.I.

THE
# ACTION OF LIGHT UPON DYED COLOURS.*
(Concluded from p. 207).

## CLASS II.—FUGITIVE COLOURS. (WOOL, *continued*).
### *Azo Colours.*
Wool Book X.
*Direct Cotton Colours.—*

9. Benzo Cyanine 3B. Constitution not published.
11. Indoin Blue 2B. From Safranine and β-naphthol.
12. Metazurin B. Constitution not published.
14. Benzo Blue 3B. Constitution not published.
15. Benzo Red Blue G. Constitution not published.
16. Columbia Blue G. Constitution not published.
17. Chicago Blue R. Constitution not published.
18. Naphthazurin. Constitution not published.
23. Diamine Blue 2B. From benzidine and amido-naphthol-disulphonic acid H.
24. Diamine Blue 3B. From tolidine and amido-naphthol disulphonic acid H.
25. Benzo Cyanine R. Constitution not published.
26. Indazurin. Constitution not published.
27. Direct Blue B. From dianisidine, dioxy-naphthoic sulphonic acid, and α-naphthol-*p*-sulphonic acid.
28. Heligoland Blue 3B. Constitution not published.
29. Benzo Azurine G. From dianisidine, and α-naphthol mono-sulphonic acid NW. S. and J. 210.
30. Benzo Red Blue R. Constitution not published.
31. Columbia Blue R. Constitution not published.
32. Benzo Azurine 3G. From dianisidine, and α-naphthol-mono-sulphonic acid L. S. and J. 213.
33. Brilliant Metazurin OOO. Constitution not published.
34. Diamine Blue BX. From tolidine, α-naphthol-mono-sulphonic acid NW, and amido-naphthol-disulphonic acid H.
35. Diamine Blue B. From ethoxy-benzidine, β-naphthol-δ-disulphonic acid, and α-naphthol-mono-sulphonic acid NW. S. and J. 205.
36. Heligoland Blue R. Constitution not published.
37. Oxamine Blue 3R. From tolidine, β-amido-α-naphthol-β-sulphonic acid, and α-naphthol-α sulphonic acid.
38. Diamine Blue 3R. From ethoxy-benzidine, and α-naphthol-mono-sulphonic acid NW. S. and J. 206.
39. Azo Blue. From tolidine, and α-naphthol-mono-sulphonic acid NW. S. and J. 187.
43. Azo Navy Blue. Constitution not published.
45. Direct Blue Black B. Constitution not published.

*Acid Colours.—*
23. Azo Acid Blue B. Constitution not published.

### *Natural Colouring Matters.*
*Mordant Colours.—*
Logwood (Al). Wood of Hæmatoxylon campechianum.

NOTES.—Azo acid blue acquires, on fading, a very red shade; turquoise blue 2B and glacier blue change to a green during the first period. Basle blue B and benzo blue 3B lose their bloom of colour during the first "fading period," the remaining dark greyish colour being moderately fast. Direct cotton colours, 12, 17, 18, 23, 24, 25, change from blue to grey during the first "fading period," and Nos. 15, 16, and 26 to 39 all acquire a marked reddish tint. On this account these colours might almost equally well be placed among the "very fugitive colours."

## CLASS III.—MODERATELY FAST COLOURS. (WOOL).
The colours of this class show distinct fading at the end of the second period (August 12 to September 3, 1895),

which becomes more pronounced at the end of the third period (September 3 to September 20, 1895). A pale tint remains at the end of the fourth period (September 20, 1895, to April 7, 1896), and at the end of a year's exposure the colour has entirely faded, or, at most, mere traces of colour remain.

### *Triphenylmethane Colours.*
Wool Book X.
*Mordant Colours.—*
1. Chrome Blue (Cr). Oxy-carboxy-tetra-methyl-diamido-diphenyl-naphthyl-carbinol.

Wool Book IX.
*Acid Colours.—*
3. Patent Blue A. Calcium salt of *m*-oxy-(or *m*-amido)-tetra-alkyl-diamido-triphenyl-carbinol - sulphonic acid.
4. Patent Blue superfine. Ditto.
12. Alkali Blue. Sodium salt of mono- and di-phenyl-rosaniline-mono-sulphonic acid.
13. Alkali Blue 6B. Sodium salt of tri-phenyl rosaniline-mono-sulphonic acid.
14. Hoechst New Blue. Calcium salts of tri-methyl-triphenyl-*p*-rosaniline, di- and tri-sulphonic acids.
15. Methyl Blue MBI. Sodium salt of tri-phenyl-*p*-rosaniline-tri-sulphonic acid.
16. Water Blue 6B extra. Sodium salt of tri-phenyl-rosaniline-tri-sulphonic acid.
17. Bavarian Blue DBF. Sodium salt of diphenylamine blue-tri-sulphonic acid. S. and J. 300.
18. Bavarian Blue DSF. Sodium salt of diphenyl-amine blue-di- and tri-sulphonic acid. S. and J. 299.
19. Alkali Blue D. Sodium salt of diphenylamine blue-mono-sulphonic acid. S. and J. 298.
20. Alkali Blue R. Sodium salt of mono-phenyl-rosaniline-mono-sulphonic acid.
22. Soluble Blue pure. Sodium salt of tri-phenyl-rosaniline-tri-sulphonic acid.

### *Oxazine Colours.*
Wool Book X.
*Mordant Colour.—*
5. Gallocyanine DH (Cr). Chloride of dimethyl-phenyl-ammonium-dioxy-phenoxazine-carboxylic acid. S. and J. 340.

Wool Book IX.
*Acid Colour.—*
35. Gallanilic Blue R. Constitution not published.

### *Induline Colours.*
Wool Book IX.
*Acid Colours.—*
26. Milling Blue. Sodium salt of anilido-iso-naphthyl-rosinduline-mono-sulphonic acid.
28. Naphthyl Blue. Sodium salt of anilido-phenyl-naphthinduline-sulphonic acid.
29. Naphthazine Blue. Sodium salt of tetra-methyl-diamido- dinaphthyl-diphenazonium-di-sulphonic acid.
30. Induline NN. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 366.
31. Indigen F liquid. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 365.
32. Induline 3B. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 366.
37. Fast Blue B. Sodium salt of sulphonic acid of a Spirit Induline. S. and J. 365.

*Basic Colours.—*
22. Toluylene Blue B. Constitution not published.
23. Indamine Blue N. Hydrochloride of *p*-amido-phenyl-amido-derivatives of a Spirit Induline.
31. Paraphenylene Blue R. Hydrochloride of amido-phenyl-induline.
32. Indophenine extra. Constitution not published.
33. Indophenine B. Constitution not published.

### Azo Colours.

Wool Book IX.
*Acid Colours.—*

38. Blue Black B. From β-naphthylamine-mono-sulphonic-acid azo-α-naphthylamine and β-naphthol-disulphonic acid R. S. and J. 134.
39. Indigo Blue powder. From toluene-azo-naphthylamine and β-naphthol-sodium-disulphonate.

Wool Book X.
*Direct Cotton Colours.—*

5. Brilliant Sulphon Azurine R. Constitution not published.
6. Sulphon Cyanine. Constitution not published.
7. Sulphon Azurine. From benzidine-sulphon-disulphonic-acid, and phenyl-β-naphthylamine. S. and J. 182.
10. Sulphon Cyanine 3R. Constitution not published.
13. Brilliant Azurine 5G. From dianisidine and dioxynaphthalene-α-mono-sulphonic acid. S. and J. 215.
19. Naphthyl Blue 2B. From o-amido-diphenylic acid, and benzoyl-amido-naphthol.
20. Benzo-Indigo Blue. From dianisidine, α-naphthylamine, and dioxy-naphthalene-α-mono-sulphonic acid (1 : 8).
21. Diamine Blue Black E. From ethoxy-benzidine, β-naphthol-δ-disulphonic acid, and γ-amido-naphthol-sulphonic acid.
22. Blue JCR. Constitution not published.
40. Benzo Black Blue R. From tolidine-disazo-α-naphthylamine and α-naphthol-mono-sulphonic acid NW. S. and J. 226.
41. Congo Fast Blue B. Constitution not published.
42. Benzo Black Blue G. From benzidine-disulphonic acid-disazo-naphthylamine, and α-naphthol-mono-sulphonic acid NW. S. and J. 225.
44. Congo Fast Blue R. Constitution not published.

### Natural Colouring Matters.

Wool Book X.
*Mordant Colour.*—Logwood (Cr). Wood of Hæmatoxylon campechianum.

NOTES.—The Patent Blues become darker during the first two fading periods. Brilliant Sulphonazurine R acquires a decided reddish tint during the later stages of fading. The Sulphocyanines and Gallocyanine DH appear to be faster than the rest of the colours placed in this class, and do not change in hue during the fading process. The fastness of the Alkali Blues is probably greater than is usually supposed to be the case. The blue given by logwood with chromium is much faster than that obtained with aluminium mordant.

### CLASS IV.—FAST COLOURS. (WOOL).

The colours of this class show comparatively little fading during the first, second, and third periods. At the end of the fourth period a pale shade remains, which at the end of the year's exposure still leaves a pale tint.

### Triphenylmethane Colours.

Wool Book X.
*Mordant Colour.—*

9. Galleïn (Cr). Oxidation product of pyrogallol-phthaleïn. S. and J. 335.

Wool Book IX.
*Basic Colour.—*

25. Gentiana Blue 6B. Hydrochloride of tri-phenyl-rosaniline.

### Oxazine Colours.

Wool Book X.
*Mordant Colour.—*

7. Gallamine Blue (Cr). Product of action of nitroso dimethyl-aniline-hydrochloride on gallaminic acid. S. and J. 346.

### Azo Colours.

Wool Book IX.
*Acid Colour.—*

36. Naphthol Blue Black. From p-nitraniline, aniline, and amido-naphthol-disulphonic acid H (1 : 8).

### Induline Colours.

*Acid Colour.—*

33. Fast Blue 6B for wool. A sulphonated induline.

NOTE.—That Gentiana Blue 6B has proved to be fast is very remarkable, since the basic colours, and particularly those of the triphenylmethane group, are usually so fugitive. During the first fading period the bloom of the colour disappears, but the remaining colour fades very little even throughout the period of a whole year.

### CLASS V.—VERY FAST COLOURS. (WOOL).

The colours of this class show a very gradual fading during the different periods, and even after a year's exposure a moderately good colour remains.

### Oxazine Colours.

Wool Book X.
*Mordant Colour.—*

6. Cœlestine Blue B (Cr). Constitution not published.

### Thiazine Colours.

*Mordant Colours.—*

10. Brilliant Alizarin Blue R (Cr). Constitution not published. A derivative of oxy-naphtho-quinone-imide.
12. Brilliant Alizarin Blue G (Cr). Constitution not published.

### Oxyketone Colours.

*Mordant Colours.—*

2. Alizarin Blue WX (Cr). Di-oxy-anthraquinone-quinoline. S. and J. 255.
3. Alizarin Blue S powder (Cr). Sodium bisulphite compound of Alizarin Blue. S. and J. 256.
4. Anthracene Blue WR (Cr). Hexa-oxy-anthraquinone.
8. Alizarin Cyanine R (Cr). Penta-oxy-anthraquinone. S. and J. 249.
11. Alizarin Cyanine G (Cr). Action of ammonia on intermediate product in making Alizarin Cyanine R. S. and J. 250.
13. Anthracene Blue WG (Cr). Constitution not published.
15. Alizarin Indigo Blue SW (Cr). Sodium bisulphite compound of tetra- and penta-oxy-anthraquinolin-quinone-sulphonic acid. S. and J. 257.
16. Alizarin Cyanine Black G (Cr). Constitution not published.

### Natural Colouring Matters.

Wool Book X.
*Direct Colour.—*

1. Vat Indigo Blue.

### Additional Colouring Matters.

*Acid Colour.—*

2. Prussian Blue.

NOTES.—The great fastness of the Brilliant Alizarin Blues is remarkable, since they belong to a group of colouring matters which has not hitherto furnished fast colours. The same remark applies to Cœlestine Blue, although this colour is not so fast as the foregoing. The fastness of the various Alizarin Blues (oxyketone colours) is proverbial, and along with the colours just named they may well be regarded as worthy competitors of indigo for the production of fast blues. The chief difference of behaviour of Indigo Blue and some of the Alizarin Blues is that the latter tend to acquire a reddish tint, whereas the former does not.

The remarkable fastness of Prussian Blue on wool is such that the medium blue colour experimented upon has not perceptibly faded during a whole year's exposure,

and it may be justly considered as the fastest blue on wool with which we are at present acquainted; unfortunately it is sensitive to the action of alkalis.

## GREEN COLOURING MATTER.

CLASS I.—VERY FUGITIVE COLOURS. (WOOL).

Wool Book XI.

*Basic Colours.—*

   1. Capri Green G. Constitution not published.

  11. Solid Green 3B. Zinc double chloride of dichlor-tetra-methyl-diamido-triphenyl-carbinol. S. and J. 265.

  13. Iodine Green. Zinc double chloride of chlor-methyl-hexa-methyl-rosaniline-hydrochloride. S. and J. 284.

  15. Methylene Green. Nitro tetra-methyl-thionine. S. and J. 349 (foot-note).

  18. Aldehyde Green. Quinoline derivative of rosaniline. (?). S. and J. 377.

*Natural Colouring Matters.*

Wool Book XI.

     Lo-kav (on cotton). Chinese dyestuff derived from Rhamnus utilis.

CLASS II.—FUGITIVE COLOURS. (WOOL).

*Triphenylmethane Colours.*

Wool Book XI.

*Acid Colours.*

   1. Light Green SF (yellow shade). Sodium salt of diethyl-dibenzyl-diamido-triphenyl-carbinol-tri-sulphonic acid. S. and J. 268.

   2. Helvetia Green. Sodium salt of tetra-methyl-diamido-tri-phenyl-carbinol-mono-sulphonic acid S. and J. 266.

   3. Light Green SF (blue shade). Sodium salt of dimethyl-dibenzyl-diamido-triphenyl-carbinol-tri-sulphonic acid. S. and J. 267.

   4. Guinea Green BV. Sodium salt of nitro-diethyl-dibenzyl-diamido-triphenyl-carbinol-di-sulphonic acid. S. and J. 270.

   5. Guinea Green B. Sodium salt of diethyl-dibenzyl-diamido-triphenyl-carbinol-di-sulphonic acid. S. and J. 269.

   9. Fast Green extra. Sodium salt of tetra-methyl-dibenzyl-pseudo-rosaniline-di-sulphonic acid. S. and J. 286.

*Basic Colours.—*

   3. Methyl Green. Zinc double chloride of chlor-methyl-hexa-methyl-$p$-rosaniline-hydro-chloride. S. and J. 283.

   4. China Green cryst. Tetra-methyl-diamido-triphenyl-carbinol oxalate. S. and J. 263.

   5. Imperial Green cryst. Zinc double chloride of tetra-methyl-diamido-triphenyl-carbinol. S. and J. 263.

   6. Solid Green GG. Tetra-methyl-diamido-triphenyl-carbinol-sulphate. S. and J. 263.

   9. Solid Green YYO cryst. Zinc double chloride of tetra-ethyl-diamido-triphenyl-carbinol. S. and J. 264.

  10. Ethyl Green cryst. Tetra-ethyl-diamido-triphenyl-carbinol-sulphate. S. and J. 264.

*Mordant Colours.—*

   2. Chrome Green (Cr). Tetra-methyl-diamido-triphenyl-carbinol-carboxylic acid.

*Safranine and Induline Colours.*

Wool Book XI.

*Basic Colours.—*

  17. Azine Green TO. Dimethyl-amido-phenyl-amido-phenyl-pheno-naphthazonium chloride. S. and J. 363.

*Azo Colours.*

Wool Book XI.

*Direct Cotton Colours.—*

   2. Columbia Green. Constitution not published.

CLASS III.—MODERATELY FAST COLOURS. (WOOL).

*Triphenylmethane Colours.*

Wool Book IX.

*Acid Colours.—*

   6. Alkali Green. Sodium salt of diphenyl-diamido-triphenyl-carbinol-mono-sulphonic acid. S. and J. 271.

   7. Wool Green S. Sodium salt of tetra-methyl-diamido-$\beta$-oxy-naphthyl-carbinol-disulphonic acid.

   8. Milling Green. Sodium salt of tetra-methyl-dibenzyl-pseudo-rosaniline-disulphonic acid.

*Azo Colours.*

Wool Book X.

*Direct Cotton Colours.—*

   1. Diamine Green B. From benzidine, $p$-nitro-benzene-azo-amido-naphthol-disulphonic acid, and phenol.

*Mordant Colours.—*

   1. Azo Green (Cr). From $m$-amido-tetra-methyl-$p$-diamido-triphenyl-methane, and salicylic acid. S. and J. 273.

CLASS IV.—FAST COLOURS. (WOOL).

Wool Book X.

*Direct Cotton Colours.—*

   3. Benzo Olive. Constitution not published.

*Mordant Colour.—*

   4. Diamond Green (Cr). Constitution not published.

CLASS V.—VERY FAST COLOURS. (WOOL).

*Triphenylmethane Colours.*

Wool Book X.

*Mordant Colours.—*

   3 . Cœruleïn (Cr). Product of the action of sulphuric acid on Galleïn. S. and J. 336.

*Oxyketone Colours.*

*Mordant Colours.—*

   5. Alizarin Green SW (Cr). Sodium bisulphite compounds of tri- and tetra-oxyanthraquinone-quinoline-sulphonic acids. S. and J. 258.

*Quinoneoxime Colours.*

*Mordant Colours.—*

   6. Dark Green (Fe). Di-quinol-dioxime. S. and J. 232.

   7. Gambine Y. (Fe). $\beta$-naphtho-quinine-$\alpha$-oxime. S. and J. 234.

   8. Gambine B (Fe). Constitution not published.

   9. Naphthol Green B (Fe). Ferrous sodium salt of nitroso-$\beta$-naphthol-$\beta$-mono-sulphonic acid. S. and J. 236.

  10. Dioxine (Fe). $\beta$-oxy-naptho-quinone-oxime. S. and J. 235.

  11. Gambine R (Fe). Naphtho-quinone-oxime. S. and J. 233.

NOTES.—The great fastness of the quinone-oxime colours when fixed with iron mordant is worthy of special notice. The fastness of Cœruleïn green as a Triphenyl-methane Colour is also remarkable, but although Cœruleïn is usually classed as a Triphenylmethane Colour, its constitution when fully determined may cause it to be more properly placed in some other class.

## SILK PATTERNS.

Most of the foregoing colours were also dyed on silk, and the patterns were exposed to light along with those on wool. The relative fastness of the various colours was, for the most part, the same as on wool, the differences observed being too unimportant to necessitate a special classification for silk.

The Chinese natural dyestuff Lo-kav fixed on silk with alum mordant is much faster than the same colour fixed on cotton from a soap bath. It was not found possible to apply it satisfactorily to wool.

Vat Indigo Blue is apparently less fast on silk than on wool, and on this fibre some of the Alizarin Blues, and notably the Brilliant Alizarin Blues, are much faster than Indigo Blue. As on wool, so on silk, Prussian Blue is faster to light than all other blues.

# NOTICES OF BOOKS.

*The Development of the Periodic Law.* By F. P. VENABLE, Ph.D., F.C.S., Professor in the University of North Carolina. Easton, Pa.: Chemical Publishing Company. 1896. 12mo. Pp. 322.

MANY readers in glancing at the title of this volume will scarcely realise all that the words convey. We may be aware that Mendeleeff and Lothar Meyer have something to do with the periodic system. But what this system includes and involves does not at first sight appear. Before we can have a periodic system, or, indeed, any system, we must have elements; we must enquire into their properties and their mutual relations. We must above all things ascertain their atomic weights, and among all these studies and researches we cannot avoid speculating on their origin. Our author, after quoting the atomic weights as according to Dalton, Wollaston, and Berzelius, enters upon the famous and much discussed hypothesis of Prout. This chemist regarded hydrogen as the primal element with the atomic weight 1, whilst the remaining atomic weights were multiples of that of hydrogen by whole numbers. But the more carefully the atomic weights were determined the more numerous become the cases not to be reconciled with this rule. It was suggested that the half the weight of H ought to be taken as the unit, and Dumas proposed to go further and take as the unit 0·25, *i.e.*, quarter the weight of hydrogen. Still difficulties occurred, and at last the fact remained that the cases where Prout's law proved to be accurate or nearly so were too numerous to be ascribed to chance. The question was raised whether we are not here in presence of a "residual phenomenon," which if eliminated or rightly estimated would justify Prout's law?

Dobereiner's triads was the next suggestion. It was pointed out that there occur analogous elements in groups of three; here the atomic weights of the extreme numbers added together and divided by two gives the atomic weight and the mean. This fact, eloquently elaborated by the great French chemist, J. B. Dumas, at the Ipswich meeting (1851) of the British Association, gave an impulse to the hopes of the transformation of the elements.

Brodie's Ideal Chemistry, sometimes referred to as the "Chemical Calculus," finds here a brief notice.

Perhaps the earliest attempt to devise a systematic and symmetrical arrangement of the whole of the elements is due to M. de Chancourtois, a French engineer. His memoir was presented to the French Academy of Science, and was duly printed in the *Comptes Rendus* for 1862 under the title "Vis tellurique, Classement naturel des Corps simples ou Radicaux obténu au moyen d'un Systeme de Classification helicoidal et numerique." This paper, although existing in such an influential and accessible form as the *Comptes Rendus*, lay dormant for thirty years, and had absolutely no influence on the development of the periodic theory. Suddenly in 1891 it was disentombed by MM. de Boisbaudran and de Lapparent under the title "Sur une Reclamation de Priorité en faveur de M. de Chancourtois relativement aux Relations numeriques des Poids Atomiques." What was the motive of the authors for keeping silence so long we have neither the right nor the opportunity of inquiring.

J. A. R. Newlands took up the subject immediately after M. de Chancourtois, but quite independently of him. The paper of Newlands when read before the Chemical Society met with a cold, not to say discourteous, reception. Subsequently the question was thoroughly and successfully re-discussed, and the claim of Newlands was vindicated. Our author here writes:—" But none of the *savants* who entered into the question ever breathed the name of de Chancourtois. His memoirs were at all times accessible in the *Comptes Rendus*. But no one found in them that meaning which MM. de Boisbaudran and Lapparent now assert. Professor Mendeleeff says—

"It is possible that Newlands has prior to me enunciated something similar to the periodic law, but even this cannot be said of Lothar Meyer." Our author, however, makes the bold assertion that "it was impossible for him (Newlands) ever to have developed the periodic law."

The merit of having effected the general recognition of this law is ascribed to Mendeleeff and Lothar Meyer. Which of these two chemists may claim the chief honour Professor Venable does not decide. Mendeleeff considered Carnelley as the only author who had added anything new to it, and denies to Meyer any part in the discovery.

The French, it is remarked, have been especially slow in acknowledging the merits of the discovery, just as in the case of Organic Evolution. Berthelot published an elaborate hostile criticism of the work of Mendeleeff, to which the latter replied in his "Faraday Lecture." Our Royal Society, on the contrary, evaded adjudicating on the respective merit of the Russian and the German chemist by awarding the Davy medal, in duplicate, to both. The position of argon and helium in the periodic scheme has given rise to some new discussion.

The diagram of the elements proposed by Reynolds and modified by Crookes avoids or rectifies some of the manifest defects of the tables of Mendeleeff and Meyer. The lecture on the "Genesis of the Elements," delivered by Mr. Crookes before the Royal Institution, merits more attention that it has received in the work before us.

It is to be remarked that Professor Venable, whilst criticising, and in general fairly, the various theories mentioned, does not give a final summing up, but leaves this delicate task to the reader. It is needless to say that the material with which he has been supplied will prove of incalculable value to the true student of the philosophy of chemistry.

We regret having to notice that the printer uses for the italic *y* and for the Greek *gamma* and *eta* a character which is not practicably distinguishable.

# CORRESPONDENCE.

## COTTON SEEDS.

*To the Editor of the Chemical News.*

SIR,—Dr. Wynter Blyth's work on Poisons is so well known, and so highly appreciated by chemists at home and abroad, that Dr. Payne has done well to call attention to an evident mistake with regard to cotton seeds. So far from being a poison, cotton seed, whether whole or decorticated, is one of the most valuable feeding stuffs at the disposal of the farmer, and at the present time cake produced by pressing the decorticated seed is selling at about five shillings per ton more than linseed cake, of which it is stated to be an adulterant.

The imports of cotton seed into the United Kingdom for the past three years have an annual value of over two million pounds sterling, the residual cake from which, after expression of the oil, would all be used for feeding purposes. In addition to this large importation of uncrushed seed there is a large quantity of cake (decorticated, undecorticated, and meal) produced from cotton seeds imported yearly, and classified in the returns as oil cake. Fully half of the imported oil cakes are derived from cotton seed, and the annual value is about £1,000,000. But notwithstanding this large consumption of cotton seed by all kinds of stock, death or injury to cattle or sheep by the use of cotton cake is of rare occurrence, and is chiefly limited to the Brazilian seed or cake, in the latter of which I have frequently found castor seed—a violently poisonous seed—in small proportions.

It seems to me, therefore, highly probable that the cases of poisoning by cotton seed recorded by Dr. Wynter Blyth have been due to a small admixture of some

poisonous seed, such as castor, and not to any poisonous principles in the cotton seed.—I am, &c.,

ALFRED SMETHAM.

16, Brunswick Street, Liverpool,
    October 19, 1896.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 15, October 12, 1896.

**Thermic Researches on Cyanamide.**—Paul Lemoult. —Cyanamide, $CNNH_2$, is a very important body on account of its relations with ureas, its constitution, and the numerous products of polymerisation to which it gives rise. It is an endothermic compound, which agrees with its great instability. It is least stable in aqueous solution, in which it behaves as an acid, the energy of which is comparable to that of HCy. It seems, therefore, that the two typical hydrogens of cyanamide are dissimilar. Both can be replaced by monovalent metals, but it is also known that the disodium salt, *e.g.*, if decomposed by water is transformed into a monometallic salt and soda.

*Bulletin de la Société d'Encouragement pour l'Industrie Nationale.* Series 5, Vol. i., No. 9.

**Complementary Notes on the Tempering of Steel.** —H. M. Have and A. Sauveur.—Translated from the *Journal of the Iron and Steel Institute.*

**Manufacture of Alumina at the Works of Larne Harbour.**—J. Sutherland.—A translation of a memoir read at a meeting of the Institution of Mechanical Engineers.

# MISCELLANEOUS.

**Bibliography of Spectroscopy.** — At the Liverpool meeting of the British Association (Section B) the Committee on the Bibliography of Spectroscopy presented an interim report to the effect that they had continued and completed the collection and classification of papers on Spectroscopy published up to the end of 1895. They originally intended to bring their work to a close with that date, but asked for reappointment in order that the compilation might be continued to the end of the century. A full report will appear next year.

**Detection and Determination of Nitrites in Water.** —MM. Barbet and Jaudrier.—A phenylendiamine cannot easily be preserved colourless ; the authors, instead, use resorcin in the following manner :—In 2 c.c. of the water to be examined they dissolve 0·1 grm. resorcin in a test-glass, and carefully superstratify upon it 1 c.c. of pure concentrated sulphuric acid. At the surface of contact of the two liquids there appears a colouration which gradually becomes more intense. It is stirred gently to and fro in order not to raise the temperature too much, and after the lapse of an hour the colour produced is compared with that obtained under the same conditions with nitrite solutions of known strength. Water containing only 1/10,000,000 sodium nitrite gives a very characteristic rose colour after the lapse of several hours. —*Journ. Pharm, und Chemie* and *Chem. Zeitung.*

# MEETINGS FOR THE WEEK.

MONDAY, Nov. 2nd.—Royal Institution, 5. General Monthly Meeting.
    — —      Society of Chemical Industry, 8. " The Production of Inoculating Materials for use in Agriculture (Nitragin)," by Dr. J. A. Voelcker, F.I.C. " The Smelting and Refining of Cyanide Bullion," by Arthur Caldecott, F.I.C.

WEDNESDAY, 4th.—Society of Public Analysts, 8. "Note on Ginger," by Thos. P. Blunt. " Determination of Stearic Acid in Fats," by Otto Hehner and C. A. Mitchell, B.A. " Further Note on Lead in Canadian Cheese," by F. Wallis Stoddart.

THURSDAY, 5th.—Chemical, 8. " The Constitution of Nitrogen Iodide," by F. D. Chattaway. B.A. "Note on the Solution and Diffusion of certain Metals in Mercury," by Prof. Roberts-Austen, C.B., F.R.S. " Compounds of Metallic Hydroxides with Iodine," by I. Rettie, B.Sc. " The Economical Preparation of Hydroxylamine Sulphate," by E. Divers, M.D., F.R.S., and Tamemasa Haga, D.Sc. " The Reduction of Nitrososulphates," by E. Divers, M.D., F.R.S., and T. Haga, D.Sc. " Amidosulphonic Acid," by E. Divers, M.D., F.R.S., and T. Haga, D.Sc. " The Molecular Conductivity of Amidosulphonic Acid," by Joji Sakurai. " Physiological Action of Amidosulphonic Acid," by Oscar Loew, Ph.D. " Imidosulphonates—Part II.," by E. Divers, M.D., F.R.S., and T. Haga, D.Sc. " How Mercurous and Mercuric Salts change into each other," by Seihachi Hada, B.Sc. " The Effect of Heat on Aqueous Solutions of Chrome Alum," by Margaret D. Dougal. " The Saponification of Ethylic Dicarboxylglutaconate," by H. W. Bolam, Ph.D. " The Periodic Law," by R. M. Deeley. " The Colouring-matters occurring in British Plants," by A. G. Perkin. " Carbohydrates of Cereal Straws," by C. F. Cross, E. J. Bevan, and Claude Smith.

# TO CORRESPONDENTS.

*L. A. Rumble.*—The book you name is a very good one. The subject is not an easy one to master.

# THE CHEMICAL NEWS.

## Vol. LXXIV., No. 1928.

### ARGON, HELIUM, AND PROUT'S HYPOTHESIS.

By BOHUSLAV BRAUNER, Ph.D., F.C.S.

THE discoverers of argon and helium, and with them the greatest majority of chemists, regard the new gases definitely as new elements, in spite of the fact that the view, according to which they are peculiar, element-like allotropic (polymeric) modifications of nitrogen and hydrogen, possesses many arguments in its favour.

As regards argon, the view that it is $N_3$ was first pronounced by Dewar, whose view was adopted and defended by new arguments by Mendeleeff, Berthelot, Lothar Meyer, Nasini, the author, and others. As regards helium, the author seems to be the only chemist who regards it as $H_3$ or $H_4$.

The chief argument that argon is a monatomic non-valent new element, with the atomic weight 39·88,—a number which is absolutely incompatible with Mendeleeff's system, — is based on the ratio of specific heats. It should be reminded that first authorities in natural philosophy do not consider the basis of this view, the kinetic theory of gases in its present form, free from objections of a very weighty character, but even, on assuming it to be absolutely correct, it is admitted by several chemists that a highly exothermic, close aggregate of three atoms without internal vibrations — non-valent —possessing only a translatory energy, will behave kinetically like a monatomic gas.

But does the vapour of mercury, the only gas upon which the analogy rests, undoubtedly consist of free single atoms?

It is generally admitted that when a gas possesses two spectra, one of them is due to a disaggregation of its molecules; and until lately this assumption did hold good for mercury, which gives and can give only one kind of spectrum. But since Eder and Valenta have shown that the vapour of mercury gives two kinds of spectra, we must assume that also mercury vapour undergoes a kind of disaggregation, and so the above argument loses much of its weight.

The second argument against argon being regarded as $N_3$ is, that its density never reaches the number, which would be in this case $d=21·06$. But nowadays, since it is not only probable that argon is a mixture, but a certainty (though the chief constituent largely prevails), the number found, $d=19·94$, must be regarded as a minimum. It has been proved by Kayser beyond all doubt, a year ago, that argon from the air of Bonn contains helium, and this fact was more recently confirmed by Friedländer (*Zeits. Phys. Chem.*, xix., 664) for the air of Berlin. If helium could not be found in English argon by its discoverers, it is easily understood in regard to the fact found by Ramsay and Collie (Ray Soc., Feb. 13), that 33 per cent of helium are invisible in the spectrum of its mixture with argon at 2·62 m.m. pressure. Now argon certainly does not contain such a large amount of helium, and, if the latter became visible to Friedländer, it was only after the greatest part of both gases had been absorbed by the metallic electrodes. Friedländer's view that argon contains only traces of helium seems unfounded, for the author was the first to show (CHEM. NEWS, lxxi., 217) how easily helium is absorbed by metallic electrodes, and its relative proportion in Friedländer's argon must have been more considerable, when some of it finally remained unabsorbed.

The recent experiment of Eder and Valenta also made it highly probable that argon is not a homogeneous body, and the separation of a heavier constituent of $d=20·01$, recently effected by Ramsay and Collie (CHEM. NEWS, lxxiv., 25), undoubtedly is an important step towards the higher limit of density.

Supposing for a moment that the hypothesis according to which argon is polymerised nitrogen be correct, we can safely say that no other properties than those of helium may be expected for similarly polymerised hydrogen, so closely is the one problem connected with the other. In helium the metallic properties of hydrogen are more developed than in ordinary hydrogen, for it is not only absorbed by electrodes, but it shows a remarkably high conductivity for electricity (Ramsay and Collie). It is true that, in accordance with the equation $A : N = He : H$, it ought to be more easily condensed than hydrogen, whereas Olszewski tried in vain to condense it at $-264°$. In the light of the classical experiments of Pictet, who showed that several bodies cannot be insulated against heat rays at low temperatures (solid chloroform fuses again when cooled below its freezing-point), it is not improbable that helium, as a good conductor of heat, is not liquefied at the lowest temperature, not parting so much with its internal energy as is necessary for the assumption of the liquid state.

A study of the specific heat of argon and helium would undoubtedly throw much light on the nature and constitutiion of these gases. It has been shown by Mendeleeff, in his classical though little-known paper "On the Law of Specific Heat, &c." (*Journ. Russ. Chem. Soc.*, ii., pp. 28 to 46, published in 1870), that, especially for "permanent" gases, the product—

$$\frac{P \cdot c}{n} = 2·4 + \frac{2}{n},$$

where $n$ = number of atoms in a molecule of the weight P—*i.e.*, the atomic heat the more approaches the constant 2·4, the more atoms are contained in a molecule. A determination of the specific heat of argon and helium would probably decide the question whether these gases are monoatomic or polyatomic, for, according to the formula $P \cdot c = n \cdot 2·4 + 2$, the molecular heat of argon would possess one of the two values, viz., $P \cdot c = 4·4$ for $A_1$ or 9·2 for $N_3$. For helium the values would be $P \cdot c = 4·4$ for $He_1$, 9·2 for $He_3$, 11·6 for $H_4$, and 14·0 for $H_5$. From this is calculated the specific heat at constant pressure for argon $c = 0·110$ or 0·231, and for helium $c = 1·1$ or 3·1 or 2·9 or 2·8.

Mendeleeff has further shown that the greatest positive difference between the atomic heat—

$$\frac{P \cdot c}{n}$$

as calculated from the specific heat found and between the atomic heat calculated from the formula—

$$\frac{P \cdot c}{n} = 2·4 + \frac{2}{n}$$

appears in the case of gases possessing a higher molecular weight, whereas the greatest negative difference is found in the case of gases, the molecular weight of which is not high when compared with the number of atoms in their molecule, so that gases of a higher molecular weight possess a higher atomic heat.

It is further seen from Mendeleeff's table that, to a certain degree even for gases, the atomic heat is a function of the atomic weight.

If argon and helium are really monoatomic gases, their atomic heat ought to be—

$$\frac{P \cdot c}{n} = 4·4;$$

if they are triatomic, their atomic heat ought to be $= 3·1$.

The values of the specific and atomic heats corresponding to the two alternatives differ so considerably from each other that we may hope that the determination

of the specific heat of the two new gases will throw new light upon the important question whether the gases are mono- or polyatomic, *i. e.*, whether they are new elements or modification of known elements.

The author, for himself, inclines to the view that argon and helium are allotropic states of nitrogen and hydrogen of a peculiar, entirely novel, character. The density of helium, $d = 2$, would correspond to a molecular weight $= 4$, and there would not be a complete analogy between helium and argon, the latter being regarded as $N_3$. But the recent classical research of Ramsay and Collie, on the separation of the constituents of helium by diffusion, makes it highly probable that the molecular weights of the two constituents in the pure state are 3 and 5. If there was some possibility of placing *one* helium with a molecular and atomic weight of $He = 4$ in the new helium-argon group of the periodic system,* it is impossible, as long as we do not give up the periodic system in its present form (which I would not feel inclined to do), to find a place for two new gaseous, monatomic, and non-valent elements between hydrogen, $H = 1$, and lithium, $Li = 7$, as well as for $A = 40$.

My modest opinion is this, that Nature has effected the synthesis of three substances which behave like elements (or, better, like simple substances, as we speak of molecules), *i. e.*, bodies which it is hitherto impossible to decompose, the molecular, and, with a certain restriction, the "atomic" weights of which equal 3, 5, and 40.† The original protylic matter (in the sense used by Crookes) of the first two element-like substances is hydrogen, and the enormously important bearing of Dr. Ramsay's discovery seems to me to lie in the point that *the constituents of helium were formed from hydrogen in accordance with Prout's law.*

The final decision of the question on the constitution of argon and helium must be left to the future ; and if the author's views on this point differ considerably from those generally adopted, he thinks it more useful for Science to discuss such important, but mysterious, problems as *open questions*, than to adopt prematurely a definite orthodox view.

Bohemian University, Prague,
    September 20, 1896.

## ESTIMATION OF SULPHUR IN ORES.
### RECLAMATION OF PRIORITY.

By Professor L. L. DE KONINCK, University of Liége.

UNDER the above title Mr. J. H. Stansbie indicates as being new the simultaneous employment of nitric acid and bromine for the oxidation of sulphur and sulphides (CHEMICAL NEWS, lxxiv., 189, 1896).

I pointed out this method in 1871 on the occasion of analysing bornite (*Bulletin de l'Académie Royale des Sciences, &c., de Belgique*, 2nd Series, T. 32, No. 11).

I reproduced it in my "Traité de Chimie analytique minérale, qualitative et quantitative," Paris and Liége, 1894, ii., 792.

Far from being new the process is more than a quarter of a century old.

Laboratoires de Chimie Analytique de l'Université de Liége.

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* I deny even this, for elements with the atomic weights 4, 20, 38, 82, &c , would have to be placed on ascending parts of Lothar Meyer's curve of atomic volumes, between H and Li, F and Na, Cl and K, Br and Rb, &c., just below the *atomic volume maxima*, where only elements like the above, *possessing the highest amount of energy of the whole period*, find their proper places, whereas the atomic volumes of such non-energetic *elements* as argon and helium must very nearly equal nought. This consideration I regard as *one of the most powerful arguments* against the view that argon and helium are new elements.

† It will be objected that three atoms of nitrogen and three or five atoms of hydrogen cannot unite according to the " laws of valency." But did protylic matter of which our elements were formed, as admitted by many chemists (a discussion of this question is promised to be held at the British Association Meeting), follow the " laws of valency ?"

## ON " TWIN-ELEMENTS."*
By RICHARD LORENZ.
(Concluded from p. 212).

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*The Distribution of all Elements upon the Series of Numbers according to the Geminal Rule.*

I WILL now consider the totality of the known elements with reference to their atomic weights and the differences of the latter as regards their distribution along the series of numbers according to the geminal rule.

As the initial point of all the chemical elements we select the atomic weights 3 and 4. These two numbers are to represent the (rounded) atomic weights of elements as yet unknown. They form a pair of twins, and indeed the first. It is named I, twin-pair I = [3, 4]. Here lies perhaps helium, the atomic weight of which is assumed 4.

According to the geminal rule, the round atomic weights of the next following pair of twins must be distinguished from those of the last mentioned by the number 4. We must therefore expect for the next pair of twins the rounded atomic weights [7, 8]. This corresponds to the nearest element known to us, lithium, with the atomic weight 7·03. This consequently occupies in the twin-group the position of the element with an odd atomic weight.

The next following theoretic pair of twins III., must again differ from the foregoing by 4 in its atomic weight. We have to expect [11, 12]. In fact the elements boron and carbon answer this requirement [11·0, 12·003].

It will be perceived that we have passed over glucinium, to which I shall return below. Several such cases will occur.

The following couple of twins, IV., = [15, 16], is not to be found, and in its place stands oxygen with the atomic weight 16·1. It corresponds to the even element of this pair.

We have again passed over an element, nitrogen.

The twin group V. must theoretically consist of elements with the atomic weights [19, 20]. In fact fluorine occupies this position ; its atomic weight, 18·99, very close upon 19, causes it to appear as the odd-numbered element of this pair. If the atomic weight of argon *is* 20, these two elements would be twins.

After fluorine follow sodium and magnesium ; in fact they form a twin group (23·058, 24·38), the atomic weights of which correspond to the twin pair VI. = [23, 24].

The following pair [27, 28] corresponds to aluminium and silicon [27·08 and 28·40].

The following elements, phosphorus and sulphur [31·03, 32·063], form the twin pair VIII. = [31, 32].

Twin-pair IX. = [35·36] corresponds to chlorine [35·453].

Then follows the pair X. It is [39·40] = K, Ca = 39·136, 40.

Next we have the twin-pair XI. [43, 44], corresponding to scandium with the atomic weight 44·09. The next twin pair, XII, [47, 48], is titanium, [48·13].

The following twin-couples are recognised as such : XIII., = 51, 52, is formed by [V, Cr = 51·21, 52·15] ; XIV. = [55, 56] by [Mn, Fe] = [56·09, 56·0]. The following twin-pair is nickel and cobalt, which, however, is displaced by about one unit from its theoretical value XV. = [59, 60]. On the other hand, we must note that the question as to the magnitude of the atomic weights of both elements is still open. After Krüss had conjectured the presence of an unknown comparison of both elements, Winkler found the atomic weight of cobalt much higher than that of nickel, whilst Hempel and Thiele obtained an inverse result.

The following twin-group, XVI., must have the atomic weights [63, 4]. This is, in fact, represented by copper, with the atomic weights, 63, 44.

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* *Zeit. Anorganische Chemie.*

The twin-pair XVII. is unknown. But we must remark that zinc (Zn = 65·38) is passed over. In like manner the following twin-pair is passed over by gallium (Ga = 69·9).

In place of the twin-pair XVIII. = [71, 72] we have germanium (72·32).

Instead of the following twin-pair, XIX. = [75, 76], comes arsenic (75·00). The next twin-group, XX. = [79, 80], is again complete [Se, Br.] = [79·07, 79·963]. The following, XXI. [83, 84], is unknown; the following, XXII. = |87, 88], is represented by strontium, rubidium having been passed over. By overleaping yttrium, zirconium, and niobium, we arrive at the twin-pair XXIV. = [95, 96], in place of which stands molybdenum (96·1). The following twin-pair, XXV. = [99, 100], is not known. If the ekamanganese predicted by Mendeleeff (atomic weight 100) exists, it represents this twin-pair. By passing over ruthenium (101·66) we arrive at rhodium (103·5) which corresponds to the twin-group XXVI. = [103, 104]. In like manner palladium and silver, 106·7, 107·938, represent the next twin group, XXXVII. = [107, 108] The next metal is cadmium (112·08), which is in the place of the twin-pair XXVIII. = [111, 112]. We must, in passing to the unknown twin-pair XXIX. =[119, 120], overleap indium.

For the twin-pair XXX. = [119, 120] we arrive at [Sn, Sb] = [119·1, 120·29]. The twin-pair XXXI. = [123, 124] is unknown; but the following, XXXII. = [127, 128], is formed by [I, Te] = [126·864, 128], where it requires to be especially noticed that the more probable succession of the two elements I, Te, which cannot be reconciled with the periodic system, is the more probable according to the geminal rule.

With the twin-pair XXXIII. we arrive at a region of elements whose atomic weights are either not accurately known or which follow other laws. These are chiefly the elements of the rare earths, including cæsium and barium. Among these the coincidences with the geminal rule are very few. The following are affected :—Cæsium, barium, lanthanum, cerium, neodymium, praseodymium, samarium, erbium, decipium, and ytterbium. Some of these elements happen in twin places, but it would be an error to lay any especial weight on this fact.

With the twin-pair XLVI. = [183, 184] a more regular succession commences. It is formed by tantalum and tungsten (182·8, 184·0). The following, XLVII. = [187, 188], is unknown. Of the next, XLVIII. = [191, 192], we know only osmium (191·6) ; indium, which doubtless belongs here, is at a greater distance (In = 193·18). The same relation occurs in the next twin-pair, XLIX. = [195, 196]. Platinum (194·83) forms one of the elements ; gold (197·25), which should form the other, is at a greater distance. There follow now only six known metals :—Hg = 200·4, Te = 204·15, Pt = 206·911, Bi = 209·0, Th = 232·4, U = 239·4. All these fall at the places required by the geminal law. Mercury represents the twin-pair L. = [199, 200], thallium the twin-pair LI. = [203, 204], lead and bismuth LII. = [207,208], thorium LVIII.=[231, 232], uranium LX. [239, 240]. It must be a surprise that lastly elements of such high atomic weight lie at the places theoretically required with the same distinctness as the earlier elements.

I may now sum up the results. The following elements, in the first place, follow the geminal rule :—He (?), Li, B, C, O, F, Ar (?), Na, Mg, Al, S, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Ge, As, Se, Br, Sr, Mo, R, Pa, Ag, Cd, Sn, Sb, I, Te. In opposition to this extremely long series of thirty-nine elements, with atomic weights of from 4 to 128, there are only ten exceptions :— H, Br, N, Zn, Ga, Rb, Y, Zr, Nb, In.

In the following part of the series the exceptions increase, especially as regards the rare earths. But even here the best known elements, and those most frequently examined, follow the geminal rule. This is verified by Ta, W, Os, Pt, Hg, Tl, Pb, Bi, Th, U, whilst Cs, Ba, Ir, Au, form important exceptions.

In the remaining elements, La, Ce, W, Pr, Sa, Er, Dp, Yb, we find some agreements and some exceptions, but these may be disregarded.

On the whole the following elements follow the geminal rules :—Helium (?), lithium, boron, carbon, oxygen, fluorine, argon (?), sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine, potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, nickel, cobalt, copper, germanium, arsenic, selenium, bromine, strontium, molybdenum, rhodium, palladium, silver, cadmium, tin, antimony, iodine, tellurium, cerium, iridium, decipium, tantalum, tungsten, osmium, platinum, mercury, thallium, lead, bismuth, thorium, uranium.

A final decision cannot be pronounced concerning those elements which, according to our present knowledge, do not agree with the regularity here discussed. It is possible that a certain part would fall in on a revision of their atomic weights. This might be especially expected in case of those elements which already approach very closely to their theoretical places. Thus lanthanum (138·5) is very near the theoretical value 139, which would form a twin-pair with cerium (140·2). The atomic weight of lanthanum is not accurately determined ; the fourth place is uncertain, and a displacement of a few tenths would bring lanthanum so near to cerium as to form a twin-pair. The case is very different where elements with well-determined atomic weights do not adapt themselves to the geminal rule. Exceptions like glucinum, nitrogen, zinc, barium, gold, &c., are very important, and for the present tell in any case against the universality of the geminal rule. But it is to be remarked that the number of exceptions is small as compared to the coincidences. Nothing compels us to assume that all the elements must follow the geminal rule. The elements may be built up in the manner of the hydrocarbons. In these the molecular weights vary by a constant difference on the access of one and the same group, e. g., = $CH_2$, If we assume this as possible for an element, it is conceivable that a series of other elements might be built up on a different plan.

## LABORATORY LAYS.

### By H. B.

To be placed amid smoking chimneys and compelled to spend month after month determining the same element in similar material is a necessity dire enough to hatch anything. The apparatus described in CHEMICAL NEWS (vol. lxxiv., p. 63) was devised to relieve a monotony, and at the same time to provide a little leisure which might be more pleasurably employed.

The modified form of an aspirator, to be described, is similarly less troublesome, and more desirable in point of accuracy than the form ordinarily employed. The principle is certainly not new, but so far as I know—and I have looked through all handy catalogues, text-books, &c.,—it has never been applied to an aspirator. In case I have been anticipated the arrangement is certainly not well known, and yet so simple and effective withal that it will bear reproduction.

During combustion a furnace tube is usually aspirated by allowing water to run from an attached bottle either clean away or into another bottle, which afterwards takes the place of the former.

The object of aspirating is to preserve the gas in the heated tube at a pressure slightly less than that of the atmosphere, so that in case a slight leak is developed the air may be drawn in rather than the contained gases or vapours pass out. When an ordinary form of gasometer is employed along with the customary aspirator, the pressure in the tube will depend on the head of water in the upper portion of the gasometer and the height of

water to be run out in the aspirator ; both these are decreasing forces, and if they act as they should at any one time, they are gradually growing weaker and weaker, and must either be readjusted time after time or permitted to act indifferently.

The apparatus shown in the figure avoid these shortcomings.* It needs no explanation, though it may be advisable to show why the suction is always constant. The tap of the tubulure having been opened the water issues from c. Through the tube P (imagine it detached from the KHO bulb) only can the air reach the inside of the bottle. The dribbling of the water from c causing the suction depends on—

Forces pushing water out of c are—

　　Weight of column of water AC + (pressure of the
　　　　atmosphere less weight of column A B on the
　　　　water in the bottle); that is the pressure of the
　　　　atmosphere—weight column BC.

Force pushing water back at c is—

　　　　Pressure of the atmosphere.

The resultant of these forces is the weight of the column BC acting downwards, and this is constant so long as B dips in the water. The length BC is adjusted so that when P is attached to the KHO bulb the air can just be pulled through the purifying train, furnace, &c.
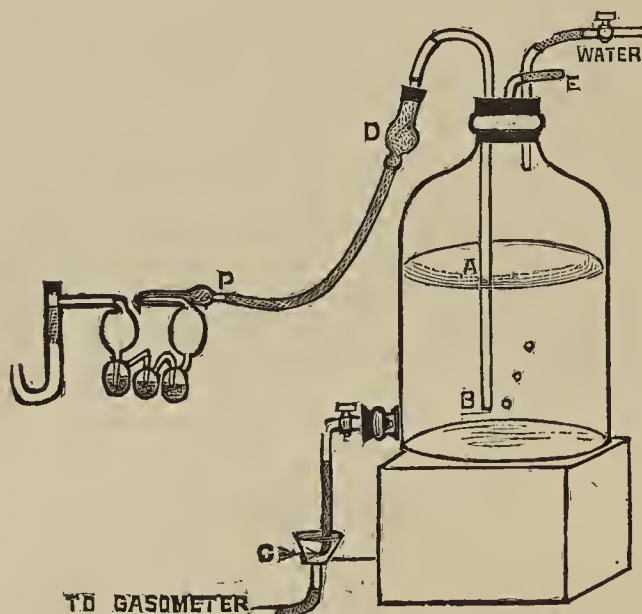


The water from c drops in the funnel, and is conveyed to the water hold of the gasometer, which stands in a cupboard underneath. If there were no combination of oxygen with carbon and no consequent absorption of $CO_2$ in the KHO, the water in the hold would preserve its level. As it is, however, it does not vary appreciably during a combustion, and very little during the consumption of the gasometer full of O.

D is filled with $CaCl_2$. The bottle is re-filled directly from a tap, and at these times the tubulure tap is closed, and the rubber cap E removed so that the displaced air may escape. When not in use either the tubulure tap or the tube E must be open, otherwise the water may rise in the tube and spoil the $CaCl_2$.

### Gas Extinguisher.

When the carbonaceous matter from a steel has been transferred to a boat it is dried in a water oven for two or three hours. It sometimes happens that they are boated just before leaving for the day, and must be burned first thing on the morrow. An arrangement for turning out the gas after a given number of hours is reproduced in CHEMICAL NEWS, lxiv., 202, from a description in the

*Chemiker Zeitung*, omitting, however, two very important particulars, viz., a perfectly constant water flow, and a means of preventing gas escape when the cistern is empty. An arrangement supplying these necessary features is the excuse to be offered for this note.

In the figure gas enters through A and leaves through B (which moves through the stopper). As soon as the water dropping from E raises the level to the lower end of B the flame is extinguished. The separatory funnel is fitted according to the principle of the preceding aspirator. The lower bottle is graduated, or the graduation may be on the movable tube B. The volume of 100 drops from the jet E is measured and marked on the bottle. If now the drops are arranged to fall at so many per minute, the volume falling in any time can be readily calculated, and the sliding tube B adjusted accordingly. The stoppers must of course be air-tight, and that being once fitted they need not again be removed—c and D are inserted so that the vessels may be respectively filled and emptied. The whole arrangement rests on a retort stand with the
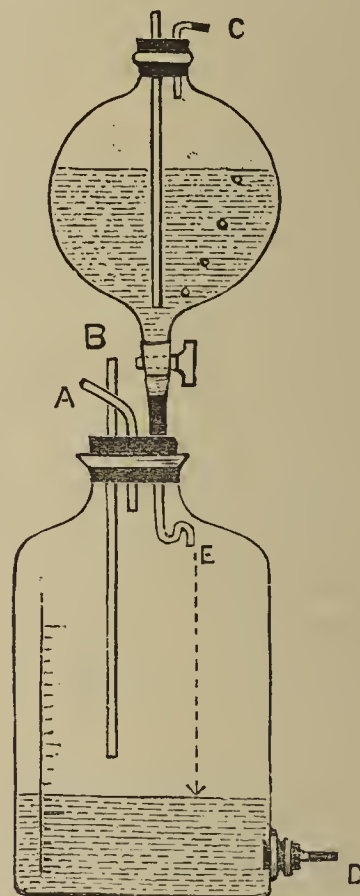


ring under the funnel. The funnel may be replaced by another aspirator bottle; such an arrangement in two trials made during the day acted in sixty-two minutes and four-and-a-quarter hours when set for sixty-one minutes and four hours respectively.

### Filtration.

A great number of experiments have been made to shorten filtering operations. Asbestos felt supported on a perforated disc in a funnel throat is always used where possible. By this means finely divided precipitate which need repeated filtering through paper are readily disposed of, but it must be noted that with very fine precipitates, when once the filtration is begun, the funnel must not be allowed to run dry or the process stopped in any other way. Neglect of this precaution often allows the precipitate to pass through. Even if the filtration be stopped by placing the finger over the end of the funnel stem the precipitate will run through when the filtration is continued. In dark coloured solutions this point may be easily overlooked, and low carbon percentages in much

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* This is not quite true of an ordinary gasometer, because the tube supplying water from the upper hold passes below the water level in the gas hold. An obvious alteration would amend this.

worked tungsten and chromium steels are often due to no other cause than this.

Asbestos may be very conveniently replaced by paper pulp, made from the clippings of soft ashless filter-paper. These devices had been used long before the admirable papers of Casamajor (CHEMICAL NEWS, xlvi., 8 ; xxxii., 33) were seen. The paper pulp filter has been much used for separating the manganese oxide after precipitation with Br and Am. The compact precipitate is not brought on to the filter until last. Having sucked the filter dry it may readily be transferred to a crucible as follows :— Lift the edge of the felt with a forcep leg, then grasp it by its clean underside and lift it boldly into the crucible. A piece of moistened filter-paper, about three-quarters of an inch square, laid on the first finger and pressed from the neck to the rim, the other hand meanwhile turning the stem, makes the funnel perfectly clean and involves less trouble than the trunicated filter-paper proposed by Casamajor. Unless the felt is laid rather thick or sucked hard, thus more or less impeding the filtration, the impact of the liquid on the new filter disturbs the pulp, and may cause a little precipitate to pass through. This may be obviated by laying a piece of filter-paper the size of a six-penny piece, on the centre of the pulp, and allowing the liquid to strike it. Our experience with felts has led us to adopt them only when the precipitate is crystalline and open, or needs little or no washing.

The rapid filtration is largely due to the power the felt has of holding the funnel stem full of water. An ordinary filter-paper acts better when this condition obtains, but it is not always, even when intended, that this happens. With small filters the following plan acts well. Fit and wet the paper as usual, then draw the paper bodily for a little way up one side of the funnel, having previously stopped the stem with the finger. When the stem has filled with water push the paper down again and remove the finger. The column of water is invariably held with a smooth funnel ; a fluted one is not so certain.

Sheffield.

# THE SEPARATION AND IDENTIFICATION OF POTASSIUM AND SODIUM.*

By D. ALBERT KREIDER and J. E. BRECKENRIDGE.

THE application of the spectroscope to the detection of potassium and sodium, for which there has thus far been no alternative, is not so unsatisfactory in the evidence as to the presence or absence of these elements as it is in its utter failure, except under delicate quantitative comparisons, to give any idea as to the quantity of either element indicated ; and since the most minute quantity of either element is sufficient to produce its characteristic line in the spectroscope, together with the fact that so many of the reagents employed in analysis contain a trace of alkali, the indication of the spectroscope is rendered misleading. While to the careful observer the presence or absence of potassium is invariably revealed, all evidence as to the ubiquitous element sodium is practically worthless. It has, therefore, appeared advisable to us to undertake the following work looking toward a method for the direct determination of sodium based upon the principle of the perchlorate method for the quantitative determination of potassium. The fact that, in the form of the perchlorate, potassium is insoluble while sodium is readily soluble in 97 per cent alcohol, affords a means for the separation of the two elements as well as for the identification of the former. By converting the sodium in the filtrate from the precipitated potassium salt either to the chloride or sulphate, in which forms it is insoluble in alcohol, a means for the detection of sodium is also provided.

Assured by the experiments previously published by one of us (Kreider, *Amer. Jour. Sci.*, xlix., 448), that the determination of potassium according to this method would be sufficiently accurate, our experimentation was directed towards determining the conditions of greatest utility and delicacy for the detection of sodium. In converting the sodium from the perchlorate to the chloride, attempts were first made to substitute some soluble chloride for the free acid, the addition of which to the alcoholic solution of sodium perchlorate it was feared might result in the formation of the dangerously explosive compound, perchloric ether. But aniline hydrochloride, prepared by saturating a solution of aniline in absolute alcohol with gaseous hydrochloric acid, when applied to the precipitation of $0.010$ grm. of sodium perchlorate dissolved in 5 c.m.$^3$ of 97 per cent alcohol, proved so hopelessly inadequate that we resorted immediately to the use of free acid, which, fortunately, was found perfectly safe even in the presence of considerable perchloric acid and at the boiling point of the mixture.

The strongest aqueous solution of hydrochloric acid, however, is inapplicable, as was proved by several experiments in which as much as $0.010$ grm. of sodium perchlorate, dissolved in only 5 c.m.$^3$ of 97 per cent alcohol, failed to be revealed by the addition of the strongest aqueous solution of the acid, added in quantities varying from a single drop to 10 c.m.$^3$—not the slightest turbidity being produced. By substituting for the aqueous solution fo the acid, a saturated solution of hydrochloric acid in 97 per cent alcohol, of which 5 c.m.$^3$ were used for the precipitation, quantities of from $0.002$ to $0.003$ grm. of sodium perchlorate dissolved in 5 c.m.$^3$ of 97 per cent alcohol could be detected with certainty ; but this could not be made sufficiently delicate. Concentrated sulphuric acid was also applied as the precipitant, and was found reliable for quantities of about $0.003$ grm. of sodium perchlorate dissolved in 10 c.m.$^3$ of 97 per cent. alcohol, when a single drop of the acid was added, but an excess of the acid caused the precipitate to re-dissolve. Gaseous hydrochloric acid proved most effectual. The dehydrating effect of the acid upon the alcohol greatly increases the insolubility of sodium and secures a remarkable delicacy, as is evident from the results recorded in Table I.

TABLE I.

| NaClO$_4$ taken. Grm. | Na$_2$O equivalent. Grm. | 97 per cent. alcohol. C.m.$^3$. | Indication. |
|---|---|---|---|
| 0·0100 | 0·00250 | 10 | very strong |
| 0·0050 | 0·00125 | 10 | strong |
| 0·0040 | 0·00100 | 10 | ,, . |
| 0·0030 | 0·00075 | 10 | ,, |
| 0·0030 | 0·00075 | 10 | good |
| 0·0020 | 0·00050 | 10 | ,, |
| 0·0020 | 0·00050 | 10 | ,, |
| 0·0010 | 0·00025 | 10 | ,, |
| 0·0005 | 0·00012 | 10 | trace |
| 0·0003 | 0·00006 | 10 | ,, |
| 0·0001 | 0·00003 | 10 | none |
| 0·0000 | 0·00000 | 10 | ,, |
| 0·0010 | 0·00025 | 40 | distinct |

The sodium employed in these determinations was in the form of perchlorate, prepared by evaporating sodium chloride, free of potassium and ammonium, with perchloric acid until tests for hydrochloric acid proved a complete conversion to the perchlorate, when the excess of acid was volatilised by heating over a drying cone. Two grms. of this purified salt were dissolved in 200 c.m.$^3$ of 97 per cent alcohol, and served for our standard solution for those tests in which quantities greater than $0.001$ grm. of sodium perchlorate were used. When it appeared evident that smaller quantities could be detected with certainty, a solution of the salt containing $0.050$ grm. per 100 c.m.$^3$ of water was used, and each portion evaporated to dryness before adding the alcohol. In each case the alcohol subsequent to its addition was saturated

with gaseous hydrochloric acid, being kept cool by immersion in a beaker of water. For the generation of hydrochloric acid, the well known form of apparatus consisting of a side neck flask, containing sodium chloride covered with hydrochloric acid fitted with a stoppered funnel, through which sulphuric acid could be admitted as desired, served admirably.

It is evident, then, that by the use of 10 c.m.³ of 97 per cent alcohol with gaseous hydrochloric acid 0·0003 grm. of sodium oxide can be found with certainty; and when the alcohol is allowed to become saturated with the gas even 0·00006 grm. of sodium oxide will be unmistakably revealed. The quantity of alcohol, 10 c.m.³, is sufficient for all purposes, since this amount will dissolve about 2 grms. of sodium perchlorate; but even in 40 c.m.³ 0·0002 grm. of sodium oxide may be seen distinctly; from which fact it is evident that this method can be applied to the quantitative determination of sodium. Absolute alcohol does not materially increase the delicacy of the test.

In Table II. are recorded the results of experiments made upon mixtures of the two elements. The sodium and potassium taken were drawn from separate standard solutions containing 1 grm. of the purified perchlorates in 100 c.m.³ of distilled water. After evaporating to dryness on the steam bath, the residue was treated with the usual amount of 97 per cent alcohol, the insoluble potassium perchlorate was removed by filtering through a dry paper filter and dry funnel into a dry test tube, and the filtrate saturated with gaseous hydrochloric acid.

TABLE II.

| $KClO_4$ taken. Grm. | $K_2O$ equivalent. Grm. | $NaClO_4$ taken. Grm. | $Na_2O$ equivalent. Grm. | Indication for potassium. | Indication for sodium. |
|---|---|---|---|---|---|
| 0·0500 | 0·01699 | 0·0500 | 0·01250 | strong | strong |
| 0·0200 | 0·00680 | 0·0200 | 0·00500 | ,, | ,, |
| 0·0100 | 0·00340 | 0·0100 | 0·00250 | ,, | ,, |
| 0·0050 | 0·00170 | 0·0050 | 0·00125 | ,, | ,, |
| 0·0040 | 0·00136 | 0·0040 | 0·00100 | good | good |
| 0·0030 | 0·00102 | 0·0030 | 0·00075 | ,, | ,, |
| 0·0020 | 0·00068 | 0·0020 | 0·00050 | ,, | ,, |
| 0·0010 | 0·00034 | 0·0010 | 0·00025 | ,, | ,, |
| 0·0005 | 0·00017 | 0·0005 | 0·00012 | trace | trace |
| 0·0003 | 0·00010 | 0·0003 | 0·00007 | ,, | ,, |
| 0·0001 | 0·00003 | 0·0001 | 0·00003 | faintest trace | none |
| 0·0000 | 0·00000 | 0·0100 | 0·00250 | none | strong |
| 0·0100 | 0·00340 | 0·0000 | 0·00000 | strong | none |

These results prove that the two elements when combined in any proportion may be separated and identified with great delicacy.

Before applying this method, however, it is necessary to remove certain interfering substances. While potassium may be safely tested for in the presence of other bases and acids, except ammonium, cæsium and rubidium, and sulphuric acid (*loc. cit.*), the large number of elements whose chlorides are insoluble in alcohol necessitates their removal before testing for sodium. But among the common alkalies ammonium is the only one whose presense is objectionable. Lithium does not affect either the test for potassium or sodium, as was determined by an experiment in which about 0·1 grm. of lithium chloride was converted into the perchlorate by evaporating with an excess of perchloric acid and treated with 10 c.m.³ of 97 per cent alcohol. A perfectly clear solution was obtained, which upon saturation with gaseous hydrochloric acid and cooling, remained clear. The removal of sulphuric acid is necessitated by the insolubility of sodium sulphate in alcohol.

TABLE III.

| Bases taken. Pb. Cu. Al. Fe. Zn. Ba. Ca, and Mg. as nitrates. Grm. | $K_2O$ taken. Grm. | $Na_2O$ taken. Grm. | Indication for potassium. | Indication for sodium. |
|---|---|---|---|---|
| 0·0500 of each | 0·0000 | 0·0000 | faintest trace | trace |
| 0·0500 ,, | 0·0017 | 0·0012 | good | good |
| 0·1000 ,, | 0·0000 | 0·0000 | faintest trace | trace |
| 0·1000 ,, | 0·0000 | 0·0005 | ,, | good |

In the experiments made with potassium and sodium associated with other acids and bases, the results of which are recorded in Table III., the following treatment was adopted. The several groups of bases were successively removed in the ordinary way: Hydrogen sulphide in ammoniacal solution removed the lead, mercury, copper, and zinc. Barium and calcium were removed by ammonium carbonate, the final filtrate being evaporated and ignited to the complete volatilisation of ammonia. The residue was dissolved and treated with barium hydrate for the removal of magnesium, and after filtering the barium was again removed by ammonium carbonate and the filtrate evaporated and ignited as before. This residue was then treated with 10 c.m.³ of boiling water, and after stirring was filtered in order to remove the organic matter usually found at this stage of the treatment. To the filtrate was added 0·1 to 0·5 c.m.³ of pure perchloric acid, about 1·7 sp. gr., according to the amount of residue, and evaporated over the steam bath until the white fumes of perchloric acid appeared. When the quantity of sodium is large it is safer to evaporate several times in order to secure a complete conversion to the perchlorate, and in such case precautions must be taken to have sufficient of the acid present. Upon treating with 97 per cent alcohol the presence of potassium is revealed by an insoluble residue. This is removed by a dry filter, and the filtrate saturated with gaseous hydrochloric acid, whereupon sodium, if originally present in amount greater than 0·0005 grm. of the oxide, will be precipitated in granular condition.

The fact that minute traces of sodium and potassium are found in the blank tests is to be expected from the delicacy of the method as proved by Tables I. and II., when it is remembered that but very few of the so-called chemically pure reagents are absolutely free of sodium, and that even distilled water kept in glass vessels contains a trace of the alkaline elements. However, the indication for sodium in the blank tests appeared only as a cloudiness, and after complete saturation, while even the quantity of sodium oxide present is not less than 0·0005, the precipitate appears in granular form and before the alcohol is completely saturated, which leaves the method all that could be desired for qualitative determinations.

*Preparation of the Perchloric Acid.*—The perchloric acid prepared according to the method previously published by one of us (Kreider, *Amer. Jour. Sci.*, xlix., 443), by converting sodium chlorate into the perchlorate by heat, destroying the residual chlorate by treating with the strongest hydrochloric acid, from which the sodium chloride was separated by filtering through a Gooch filter and the excess of hydrochloric acid removed by evaporation—while answering perfectly well for the detection of potassium, is inapplicable to the test for sodium, because of the small amount of this element which the acid always contains, due to the partial solubility of sodium chloride in hydrochloric acid. As distillation seems the only method for the removal of this residual sodium, our attention was given to a study of the best conditions for the distillation. Various experiments led to the adoption of the following treatment, which we found in every case perfectly safe and fairly rapid. To prevent loss by decomposition the distillation must be carried on under diminished pressure, and unless the acid has been previously concentrated by evaporating until the white fumes appear, if there is any considerable amount of the acid in the distilling flask, even with porcelain chips to check it, it bumps with such violence as to throw the liquid to all parts of the flask and possibly into the condenser. It appeared to be essential, therefore, to start with only a small amount of the concentrated acid in an apparatus which would permit of the gradual addition of the acid without relieving the vacuum. Rubber stoppers or connectors are not advisably used where the acid may condense upon them and flow back into the flask. Invariably oxidisable matter is carried back, causing explosions

which vary in force and seriousness according to circumstances.

We, therefore, selected a strong distilling flask of about 100 c.m.³ capacity, and sealed into the tubulation a stoppered funnel which reached well into the bulb. The stop-cock of this funnel was carefully cleansed of vaseline and lubricated with metaphosphoric acid obtained by boiling syrupy orthophosphoric acid until the temperature of 350° C. has been attained.* The side neck of the flask was inclined upward for a short distance before being bent into the receiver, with which it was connected by a rubber stopper through which the tube extended for a safe distance. An ordinary bottle of 250 c.m.³ capacity served for a receiver, and was closed by a doubly perforated stopper. Through one of the perforations the adapter from the condenser was entered; through the other connection was made with a small glass bulb inserted between the receiver and the next tube, containing moistened sticks of caustic potash, in order to prevent the potash from reaching the receiver in case of an accident to the pump. The object of the potash was to absorb any chlorine resulting from the inevitable slight decomposition of the acid, and thus to protect the mercury of the pump. For the exhaustion an automatic pump was employed, and generally twenty minutes would suffice to reduce the pressure to about 8 m.m., when the distillation was begun. The pump gradually reduced the pressure, which was kept at about 3 to 5 m.m. The bottom of the distilling flask was covered with a layer of fine porcelain chips to a depth of about 1 c.m.³, and the whole flask was surrounded by a cylinder of thin sheet iron closed below, while the upper opening was protected by an asbestos cover. By this means heat was uniformly applied to every part of the flask and up to the point at which, if the acid condensed, it would flow into the receiver. Three or 4 c.m.³ of the acid were admitted to the flask, after which the temperature was raised to about 130° C. and the acid admitted at about the same rate that it dropped from the condenser, care being taken to prevent the liquid in the distilling flask from disappearing entirely. No danger was experienced in admitting the acid; the porcelain chips distribute the heat and prevent the colder acid from reaching the glass.

Careful compliance with the above conditions will secure satisfactory results. As a rule we succeeded in distilling at the rate of 25 c.m.³ to 40 c.m.³ per hour, and when it is remembered that the product is the dihydrate of perchloric acid, the most concentrated form in which it is stable, and of which 0·1 grm. of potassium oxide requires only 0·16 c.m.³, it will be seen that by this process the acid may be prepared without great difficulty.

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## DETERMINATION OF URIC ACID IN GUANO.†

### By A. STUTZER and A. KARLOWA.

For a long time past guano imported from Peru has been comparatively poor in uric acid; of late, however, cargoes have arrived equalling in quality the best shipped during the fifties; the determination of the quantity of uric acid present in these new shipments is, therefore, of some interest. We endeavoured to find a method for its determination, and the following seemed likely to be suitable.

A good average sample of the guano is reduced to fine powder and, if rich in nitrogen, 1 grm., or if poor, 2 grms., taken for the determination. This is placed in a porcelain basin, some water added, and then

hydrochloric acid to slight acid reaction. The liquid is evaporated on the water-bath until all hydrochloric acid is expelled, 100 c.c. of water, containing 3 grms. of piperazine in solution, added, and the whole boiled for about a minute. It is then filtered, cooled, a little phenolphthalein added, and just sufficient hydrochloric acid to correct the alkaline reaction; 10 c.c. of a 10 per cent hydrochloric acid solution are now added, the solution well stirred (preferably by the aid of a stirring machine), and allowed to stand for 12 hours. The separated crystals of uric acid are collected upon a filter of known (but lowest possible) percentage of nitrogen, and washed with water containing 1 per cent hydrochloric acid, until the filtrate and washings together amount to 200 c.c. With the filter and its contents a nitrogen determination is made, and the percentage of uric acid calculated from the nitrogen found, 1 part being equal to 2·994 parts uric acid.

It was necessary, however, in the first place to determine the solubility of uric acid in a 1 per cent hydrochloric acid solution, in order to establish the proper correction for solubility. We obtained for this purpose a specimen of the purest commercial uric acid—a fine white powder—and found that 100 c.c. of the 1 per cent hydrochloric acid solution were capable of dissolving at the mean temperature of the room 0·0084 grm. uric acid, an amount represented by the proportion 1 : 11890. We obtained quite different figures, however, on experimenting with uric acid in the crystalline state. Some uric acid was dissolved in piperazine, separated, as before described, with hydrochloric acid, filtered after standing for twenty-four hours, washed with water, and dried at 100° C. The analysis showed 33·30 per cent nitrogen, as against 33·31 per cent required by theory. Determinations made with this preparation showed that it dissolved with much greater difficulty, only 1 part in 43,478. The 100 c.c. dissolved 0·0023 grm. We are only able to explain this difference by attributing it to the crystalline structure of the uric acid, for as the commercial specimen first used was also pure according to chemical analysis, the only difference between the two preparations was that of physical character.

In making use of this method we have to calculate the solubility upon 200 c.c. of filtrate. It is, however, only the first 100 c.c. that can be considered as saturated with uric acid; the washings contain less. If, therefore, we assume that the 200 c.c. of filtrate and washings contain 0·003 grm. uric acid, and we add this amount to the results obtained, we make the nearest approximation to the truth.

We found in a sample of Chinchas Peruvian guano, imported by the Anglo-Continental Guano Works, Hamburg, 27·60 per cent uric acid, other constituents of manurial value being also present, as follows:—

| Phosphoric acid soluble in citrate by P. | | |
|---|---|---|
| Wagner's method .. .. .. .. .. | 9·25 | per cent |
| Total phosphoric acid .. .. .. .. .. | 9·60 | ,, |
| Nitrogen in the form of uric acid .. .. | 9·20 | ,, |
| Nitrogen in other organic forms .. .. | 4·00 | ,, |
| Nitrogen in the form of ammonia .. .. | 2·10 | ,, |
| Total nitrogen .. .. .. .. .. .. | 15·30 | ,, |

In another sample of Chinchas guano we found 23·82 per cent uric acid and the following other manurial constituents:—

| Phosphoric acid soluble in water .. .. | 3·32 | per cent |
|---|---|---|
| Phosphoric acid soluble in citrate by Wagner's method (which includes that soluble in water) .. .. .. .. .. | 8·54 | ,, |
| Total phosphoric acid .. .. .. .. .. | 10·37 | ,, |
| Potash .. .. .. .. .. .. .. .. | 2·41 | ,, |
| Nitrogen in the form of uric acid .. .. | 7·96 | ,, |
| Nitrogen in other organic forms .. .. | 4·21 | ,, |
| Nitrogen in the form of ammonia .. .. | 2·30 | ,, |
| Total nitrogen .. .. .. .. .. .. | 14·47 | ,, |

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* This lubricant will be found entirely satisfactory and greatly preferable to vaseline in many other operations where the greasy effect of the latter is objectionable.

† *Chemiker Zeitung*, xx., 721.

The quantity of uric acid present in these guanos is noteworthy. Whether the method used for its determination would also be suitable for the analysis of other substances we have not yet ascertained.

## NOTE ON USE OF GEISSLER FILTER-PUMP AS AN ASPIRATOR.

### By E. G. BYRANT.

THE glass pump is connected to a water tap as usual, the suction tube being attached to any apparatus through which a current of air is required. The current can be thus easily made continuous and of any desired rapidity. Moreover, by means of a short piece of indiarubber tubing at the bottom of the pump, specimens of the aspirated air can be collected at a pneumatic trough provided with overflow.

## THE PRESENCE OF NITRITES IN THE AIR.*

### By GEORGE DEFREN, M.S.

IT is well known that the atmospheric air contains, besides its main normal constituents, oxygen and nitrogen, admixtures in varying quantities of not only carbon dioxide and aqueous vapour, but, especially in the neighbourhood of cities (Mabery and Snyder, *Journ. Am. Chem. Soc.*, xvii., 105), ammonia and various gases arising from industrial processes and resulting from the decomposition of animal and vegetable life.

The amounts of the impurities in the air may be very small. Ammonia exists sometimes to the extent of one part in 1,000,000. Ozone is said to be produced by electrical discharges during storms, by the breaking of waves on rocks, and other causes (Gorup V. Besanez, *Ann. Chem. Pharm.*, clxi., 232). It has been shown (Carius, *Ber. Deut. Chem. Gesell.*, viii., 1481) that when ammonia and ozone unite in the air they form hydrogen peroxide, ammonium nitrite, and ammonium nitrate. It has also been observed (Goppelsroder, *Jour. f. Prakt. Chem.* [2], iv., 139, 383; Smith "On Air and Rain," 438; Bechi, *Ber. Deut. Chem. Gesell.*, viii., 1203) that rain obtained during thunder-storms contained more nitrites and nitrates than ordinary rain, from which we conclude that electrical discharges have some effect on this combination.

Aside from the above several investigations have been carried out to determine the origin of nitrites in the air and the possible effect of these nitrites on the human system. Boke (CHEM. NEWS, xxii., 57) claims that when illuminating gas is burned the higher oxides of nitrogen are formed. W. V. Hoffmann (*Ber. Deut. Chem. Gesell.*, 1870, 658) noticed that on combustion a gas was formed which had a reddish colour and possessed an odour resembling that of nitrous acid. E. A. Greete and P. Zoeller showed (*Ber. Deut. Chem. Gesell.*, 1877, 2144 b), by a conclusive investigation, that when absolutely pure hydrogen was burned in pure air the condensed water formed showed an appreciable quantity of nitrous acid by the use of Griess's reagent. Berthelot (*Comptes Rendus*, lxxxix., 882) and Stohmann (*Jour. f. Prakt. Chem.*, xix., 142) found that by the combustion of nitrogenous bodies nitrous, nitric, and hyponitrous acids were formed. Leens (*Am. Chem. Soc. J.*, 1884, 3), Wurster (*Ber. Deut. Chem. Gesell.*, 1886, 3202, 3206), and Wright (*Chem. Soc. J.*, xxxvii., 422; CHEM. NEWS, xli., 169; *Chem. Ind.*, 1880, 207) also found nitrous acid as a product of the combustion of illuminating gas. Louis Ilosvay de N. Ilosva (*Bull. Soc. Chem. d. Par.*, 1889, ii., 377; *Ber. Deut. Chem. Gesell.*, 1889, 793) made extensive researches on the subject, and came to the conclusion that the higher oxides of nitrogen were formed, but that no ozone nor hydrogen peroxide could be obtained. The presence of hydrogen peroxide

in snow and rain (Schöne, *Ber. Deut. Chem. Gesell.*, vii., 1695) was due to other causes. Finally, Alfred Von Bibra (*Archiv f. Hygiene*, xv., 216) investigated the question, and obtained considerable nitrous acid when illuminating gas was burned. Mabery and Snyder (*Jour. Am. Chem. Soc.*, xvii., 121) have recently determined the amounts of nitrites found in air in various localities.

That headache and depression are experienced in crowded rooms is universally recognised, but the exact cause is not yet clearly determined. Formerly the presence of excessive carbon dioxide was supposed to be sufficient to account for the evil effects of bad air, but the researches of Hammond, Brown-Sequard, and D'Arsonval (*Comptes Rendus*, 1888, 33; *Société de Biol.*, 99, 99, 108, 110), and Merkel (*Archiv f. Hygiene*, xv., 1), claim the presence of a volatile organic poison in the fluid condensed from expired air. The results, however, have been contested by Dostre and Loye (*Comptes Rendus*, lxxxviii., 91—99), Russo Gilibert and Alessi (*Boletino della Società d'Igiene di Palermo*, lxxxviii., Nr. 9), Hofmann-Wellenhof (*Wiener Klinische Wochenschrift*, lxxxviii., Nr. 37) Lehmann and Jessen, (*Archiv f. Hygiene*, x., 267), Bergey, Mitchell, and Billings (" Report to Smithsonian Institution"; *Nat. Acad. Science*, April 16, 1895; *Science*, New Series, i., 481, 482). The latter-named investigators claim that the injurious effects of air expired from the lungs appear to be due entirely to the diminution of oxygen or increase in carbon dioxide, or to a combination of these two factors, and state that it is improbable that the minute quantity of organic matter contained in expired air has any deleterious influence on men who inhale it in crowded rooms.

Even if no organic poison be exhaled from the lungs it is nevertheless a fact (Merkel, *loc. cit.*) that mice placed in closed receptacles and forced to breathe the expired air from other mice quickly died, showing the presence of some harmful substance. In direct connection with this observation stand the results obtained by Falck (*Lehrbuch d. Prakt. Toxicologie*, 1880, S. 64), Husemann (*Lehrbuch d. Toxicologie*), Charier (*Bull. de la Soc. Med. d'Emulat*, 1823), Sucquet (*Jour. d. Med.*, 1860), Desgranges (*Jour. d. Med.*, T. 8), Eulenberg (*Die Lehre von d. gift Gasen*, 1865, 251), Purcell (*Med. and Surg. Report*, 1872, p. 313), Schmitz (*Berl. kl. W. Schr.*, 1883, S. 428; 1884, S. 335), and Pott (*D. Med. Woch.*, 1884, 29, 30), on the poisonous qualities of nitrous acid.

With the more delicate methods of determining nitrites it has been proved that they exist in the air of inhabited rooms: hence the question naturally arises, Could the presence of *nitrites* in the air exert any influence in causing the effects hitherto wholly attributed to the carbonic acid gas? Ilosvay (*loc. cit.*, *Ber.*, 798 c.; *Bull. Soc. Chem.*, 388—391) claims that nitrites are exhaled from the lungs, and Wurster (*Ber. Dent. Chem. Gesell.*, 1886, 3202, 3206) and Cramer (*Jour. f. Gasbeleucht u. Wasserversorg*, 1891, 65; *Archiv f. Hygiene*, 10, 321) maintain that the nitrites formed by the combustion of illuminating gas are the direct cause of the depressed feeling and uneasiness experienced in crowded rooms, while Rübner shows (*Archiv f. Hygiene*, xvi., 101) that the humidity and rise of temperature possess an appreciable influence on the animal organism.

Comparatively little attention has been paid to the quantity of nitrites present in the air of inhabited rooms, and directions for these compounds are not available for the general student. The object of the work here reported was to show that nitrites do exist in the air in appreciable though small quantity, that the amount of nitrites is varying under varying conditions, and that they increase in the same manner and under like circumstances as does carbon dioxide, thus indicating that they are products of combustion.

That nitrites do exist in the air of rooms is evident from the fact that 100 c.c. of pure water, treated with a mixture of 1 c.c. hydrochloric acid (1 : 4), 2 c.c. sulphanilic acid, and 2 c.c. naphthylamine hydrochlorate solution, and

exposed to the air, rapidly takes on a deep pink colour, due to the absorption of nitrites from the air by the water, forming α - naphthylamine - azo - benzenesulphonic acid. For this reason the various "standards" used in estimating the amounts of nitrites in water are always freshly prepared on making an analysis to prevent as much as possible any liability of error in the determination.

The work described below was carried on in the Walker Building of the Massachusetts Institute of Technology. This structure has the reputation of being one of the best ventilated in the conntry, the air in the laboratories being completely changed once in seven minutes, so that some of the results obtained will be somewhat different from those possible in places where not so much attention is given to obtaining a good supply of fresh air.

The first experiment tried was to determine the rate of absorption of nitrites by water in various laboratories. 100 c.c. of re-distilled water were placed in each of three porcelain evaporating dishes (15 c.m. in diameter), which gave in each case a superficial area of water exposed to the air of about 95 sq. c.m. These were then allowed to stand for specified times in a room, and the amounts of nitrites absorbed by the water determined in the usual manner. The re-distilled water used was that employed by the Massachusetts State Board of Health in making its various standards for determining the amounts of ammonia, nitrites, and nitrates, thus insuring the freedom of the water from these substances.

The absorption of nitrites by water in Room 36, Walker Building, was first determined. During the day on which this experiment was carried on no water analyses were in progress. One gas burner had been in use a part of the morning. In the latter part of the afternoon two lamps were burning till after five o'clock. An apparatus for furnishing hot water, heated by means of gas, was put into service at 3.30 p.m., and left burning till after five o'clock. In this room there were also, on an average, three persons employed during the day.

The three porcelain dishes containing each 100 c.c. of best re-distilled water, free from nitrites, were placed side by side on a desk and exposed to the air for varying lengths of time, being then treated with the reagents named above, the depth of colour produced by this means being compared to that of standard potassium nitrite solutions (1 c.c. containing 0·0000001 grm. nitrogen as nitrite) treated with the same reagents.

An analogous experiment was tried in Room 38 of the same building. During the morning one lamp had been burning one hour. Work was carried on by three persons during various portions of the day, they, however, not requiring the use of any gas burners. The three porcelain dishes were placed in position on a desk at two o'clock in the same manner as in the preceding case.

The third trial of the series was made with the air in Room 39. Four Bunsen burners had been in use all day, being turned out at five o'clock. Three students had been at work the greater part of the time, and at occasional intervals others were also present. The first two samples of water were placed in position at 2 p.m., and the third, which was exposed for seventeen hours, was placed in position at 4 p.m. The results of these series of experiments are given in the following table :—

*Hours of Exposure.*

| Room. | 1. | 2. | 17. | 19. |
|---|---|---|---|---|
| | | C.c. equivalent nitrite solution. | | |
| 36 | 2·5 | 3·5 | — | 57·2 |
| 38 | 3·5 | 8·5 | — | 72·7 |
| 39 | 8·0 | 13·5 | 84·2 | — |

On examining the above results we notice the following :—

1. Even in the air of the best ventilated rooms where gas is burned nitrites exist.

2. Water exposed undisturbed to the air absorbs nitrites there existing.

3. The amount of nitrites so absorbed increases in almost direct proportion to the time the water is exposed, being also dependent, however, on the nature of the work carried on in the room.

4. On burning illuminating gas some of the nitrogenous constituents, though small in amount, are incompletely oxidised to nitrites.

(To be continued).

## ON THE INVERSION OF SUGAR BY SALTS.*
### No. II.
#### By J. H. LONG.
(Continued from p. 216).

*Ammonium Ferrous Sulphate.*

BUT one experiment was made with this salt, a very nice crystallised preparation was used.

*Experiment 8.*

$(NH_4)_2Fe(SO_4)_2.6H_4O.$   N/2.

In 500 c.c., 100 grms. of sugar + 49 grms. of sulphate.
A = 17·08.

| $t.$ | $a.$ | $x.$ | $\text{Log.} \frac{A}{A-x}.$ | $\frac{1}{t}\log.\frac{A}{A-x}$ |
|---|---|---|---|---|
| 0 | 12·93° | — | — | — |
| 17 | 12·49 | 0·44° | 0·01134 | 0·00066 |
| 45 | 11·74 | 1·19 | 0·03137 | 0·00069 |
| 75 | 10·93 | 2·00 | 0·05409 | 0·00072 |
| 105 | 10·13 | 2·80 | 0·07776 | 0·00074 |
| 165 | 8·60 | 4·33 | 0·12698 | 0·00077 |
| 225 | 7·30 | 5·63 | 0·17368 | 0·00077 |
| 345 | 4·60 | 8·33 | 0·29048 | 0·00084 |
| 465 | 2·85 | 10·08 | 0·38739 | 0·00083 |
| 525 | 2·20 | 10·73 | 0·42972 | 0·00082 |
| | | | | 0·00076 |

The coefficient is seen to be low, but nearly a constant. In this case, as in that of the ferrous sulphate, the mixture became slightly turbid on heating.

*Zinc Sulphate.*

It is practically difficult to secure a good preparation of zinc sulphate crystallised without the addition of a trace of sulphuric acid. In absence of the acid crystallisation is very slow. The preparation used below was made from a chemically pure commercial sample, by crystallising with a trace of acid first and then from pure water, after heating the solution with pure zinc. The final crystallisation, to secure 50 grms., required weeks for its completion. In my former paper attention was called to the fact that inversion with zinc sulphate is very slow, which is well shown below. The experiment was closed when the sugar was about half inverted, and as the coefficient is not regular, it is not possible to estimate accurately the mean rate for the whole period.

*Experiment 9.*

$ZnSO_4.7H_2O.$   N/2.

In 250 c.c., 50 grms. of sugar + 17·94 grms. of the sulphate.
A = 17·25.

| 0 | 13·10 | — | — | — |
|---|---|---|---|---|
| 15 | 12·88 | 0·22° | 0·00558 | 0·00037 |
| 45 | 12·35 | 0·75 | 0·01935 | 0·00043 |
| 105 | 11·34 | 1·76 | 0·04674 | 0·00044 |
| 165 | 10·40 | 2·70 | 0·07393 | 0·00045 |
| 285 | 8·48 | 4·62 | 0·13539 | 0·00048 |
| 405 | 6·51 | 6·59 | 0·20903 | 0·00052 |
| 525 | 4·68 | 8·42 | 0·29083 | 0·00055 |

### Manganous Sulphate.

After several attempts a salt was obtained crystallised from perfectly neutral solution. Some of the crystals were so irregular in outline that it was not possible to determine from inspection whether they contained 4 or 5 molecules of water. Determination of $SO_4$ in the product showed, however, that a very small amount only of the latter salt was present. In making the solutions I assumed for convenience that the compound had the formula $MnSO_4 \cdot 4H_2O$, and weighed out accordingly.

As I pointed out in my former paper, a solution of manganous sulphate and sugar undergoes a peculiar decomposition when heated, in which a very fine dark substance is thrown out from solution. The amount of this is so small that I could not collect enough for tests in the work done; but it is still sufficient to make the polarimeter readings very difficult. All solutions had to be filtered before examination, but even with this precaution the readings were often obscure.

### Experiment 10.

$MnSO_4 \cdot 4H_2O$.　N/2.

In 250 c.c., 50 grms. of sugar $+$ 13·94 grms. of sulphate.

A = 34·80.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 26·50° | — | — | — |
| 45 | 26·33 | 0·17° | 0·00213 | 0·000047 |
| 75 | 26·15 | 0·35 | 0·00439 | 0·000058 |
| 135 | 25·76 | 0·74 | 0·00934 | 0·000069 |
| 195 | 25·05 | 1·45 | 0·01848 | 0·000095 |
| 315 | 22·33 | 4·17 | 0·05543 | 0·000176 |
| 435 | 19·84 | 6·66 | 0·09226 | 0·000212 |
| 555 | 16·75 | 9·75 | 0·14277 | 0·000257 |

### Experiment 11.

$MnSO_4 \cdot 4H_2O$.　N.

In 250 c.c., 50 grms. of sugar $+$ 27·88 grms. of sulphate.

A = 34·75.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 26·45° | — | — | — |
| 15 | 26·25 | 0·20° | 0·00250 | 0·00017 |
| 45 | 26·00 | 0·45 | 0·00566 | 0·00013 |
| 75 | 25·75 | 0·70 | 0·00883 | 0·00012 |
| 135 | 24·90 | 1·55 | 0·01981 | 0·00015 |
| 195 | 23·00 | 3·45 | 1·04541 | 0·00023 |
| 315 | 18·20 | 8·25 | 0·11770 | 0·00037 |
| 435 | 14·45 | 12·00 | 0·18397 | 0·00042 |
| 555 | 9·50 | 16 95 | 0·29053 | 0·00052 |

### Experiment 12.

$MnSO_4 \cdot 4H_2O$.　2N.

In 250 c.c., 50 grms. of sugar $+$ 55·76 grms. of sulphate.

A = 34·42.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 26·12° | — | — | — |
| 30 | 25·12 | 1·00° | 0·01280 | 0·00043 |
| 90 | 22·80 | 3·32 | 0·04405 | 0·00049 |
| 150 | 17·82 | 8·30 | 0·11984 | 0·00080 |
| 220 | 12·33 | 13·79 | 0·22231 | 0 00101 |
| 338 | 4·60 | 21·52 | 0·42622 | 0·00126 |
| 450 | 0·27 | 25·85 | 0·60383 | 0·00134 |
| 570 | −3·80 | 29·92 | 0·88360 | 0·00155 |

### Experiment 13.

$MnSO_4 \cdot 4H_2O$.　3N.

In 250 c.c., 50 grms. of sugar $+$ 83·64 grms. of sulphate.

A = 34·00.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 25·70° | — | — | — |
| 30 | 24·22 | 1·48° | 0·01933 | 0·00064 |
| 90 | 18·76 | 6·94 | 0·09915 | 0·00110 |
| 150 | 11·50 | 14·20 | 0·23481 | 0·00156 |
| 220 | 4·75 | 20·95 | 0·41587 | 0·00189 |
| 338 | −2·69 | 28·39 | 0·78252 | 0·00232 |
| 450 | −6·25 | 31·96 | 1·22185 | 0·00272 |
| 570 | −8·05 | 33·75 | 2·13354 | 0·00363 |

The rates of inversion cannot be directly compared in the above experiments because the latter were not carried to completion. In the first case over one-third of the sugar originally present was inverted; in the second case almost exactly one-half; in the third case about six-sevenths; while in the last case the inversion was very nearly complete. By plotting the results it is possible to determine approximately the rate of inversion when just one-half of the sugar has been inverted, and this I have done. The results are given below, and show that the coefficients, K, are nearly proportional to the concentrations, these being referred to that of the half-normal solution as unity.

| Conc. | K. |
|---|---|
| 1 | (0 00032) |
| 2 | 0·00054 |
| 4 | 0·00109 |
| 6 | 0·00172 |

The first coefficient (0·00032) is uncertain because it was found by a rather wide extrapolation, but between the others there is fair agreement.

(To be continued).

# PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY.

*Special General Meeting, October 30th, 1896.*

Captain ABNEY, President, in the Chair.

THE Secretary having read a summary of the replies sent by Members to a circular which had been addressed to them during the last Session, a series of Resolutions drawn up by the Council bearing on the points raised by this circular were adopted. The chief of these Resolutions were to the following effect: — (1) That the subscription to the Society be raised to £2 2s. (2) That present Life Members be invited to voluntarily subscribe £1 1s. annually to the funds of the Society, or to compound for this annual contribution. (3) That a guarantee fund be instituted. (4) That in future Members of the Society be styled Fellows of the Physical Society of London.

In the course of the discussion on these Resolutions the President, Secretary, and Treasurer gave an account of the financial position of the Society, and explained that at present each Member receives from the Society, in the shape of Proceedings and Abstracts, printed matter which costs the Society more than the amount of the annual subscription.

The *Ordinary Science Meeting* was then held.

A letter was read from Lord Kelvin thanking the Society for the Address which the President, on their behalf, had recently presented to him.

Prof. W. STROUD read a paper, by himself and Mr. J. B. HENDERSON, on a "*Satisfactory Method of Measuring Electrolytic Conductivity by means of Continuous Currents.*"

The method consists in placing a balancing electrolytic cell in the arm of the Wheatstone's bridge adjacent to the arm containing the chief electrolytic cell, so that the electromotive force of polarisation in the two cells neutralise each other's effect on the galvanometer. The authors find that if the resistance of the arms of the bridge are high (20,000 ohms), and if an E.M.F. of about 30 volts is used in the battery circuit, then the resistance of a solution (of potassium chlorate in their experiments) can be determined to within about one part in two thousand. With a D'Arsonval galvanometer the balancing cell is so efficacious that it is impossible to tell that it is not a metallic resistance that is being measured.

Prof. PERRY asked if the authors had tested whether the difference in resistance of the two cells was pro-

portional to the difference in length of the liquid columns.

Mr. APPLEYARD said he had found that the resistance of an electrolyte appeared to vary, because in the ordinary arrangement the cell was short circuited through the arms of the bridge. He suggested as a remedy the making and breaking of the circuit by a special key, so arranged that except when taking a reading the cell is on open circuit.

Mr. BLAKESLEY asked if the authors had tried the method in which the resistances are adjusted till, when the battery circuit is broken, there is no immediate change in the galvanometer deflection. It is possible by this method to measure a resistance of between 6,000 and 10,000 ohms to within 0·1 per cent.

Prof. AYRTON said the method referred to by Mr. Blakesley was the ordinary "false zero" method. In using this method you were working to a continuously altering zero; in Prof. Stroud's method, however, the zero was constant.

Mr. APPLEYARD said he had found the "false zero" method troublesome to use.

Prof. STROUD, in reply, said they had not tested the proportionality between the resistance and length, and they had not tried the "false zero" method.

Mr. APPLEYARD then exhibited a number of different forms of Electrical Trevelyan Rockers.

The most interesting one consisted of two rods of carbon fixed to a wooden sounding-board, with a third carbon rod lying across the other two so as to form a microphone. A fairly strong current is passed through this microphone, and through two electro-magnets which act on the prongs of a tuning-fork fixed to the sounding-board. The tuning-fork acts on the microphone, which, by making and breaking the current, keeps the fork in vibration.

A cylinder of carbon, forming the "knife-edge" of a small pendulum supported on two horizontal carbon rods, kept the pendulum in violent oscillation as long as a current passed from one of the horizontal rods, through the movable cylinder and out through the other horizontal rod.

The Society then adjourned till November 13th.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 16, October 19, 1896.

New Researches on the Decomposition of Sugars under the Influence of Acids, and especially on the Production of Carbonic Acid.—MM. Berthelot and G. André.—This paper will be given at some extent as early as possible.

Comparative Digestibility of Cocoa-nut Butter and Cows' Butter.—In a course of experiments it appeared that the digestibility of vegetable butter (that obtained from the cocoa-nut) is 98 per cent, whilst that of cows' butter (*i.e.*, that obtained from the milk of the cow) is 95·8 per cent.

Certain Coloured Reactions of Brucine; Researches on Nitrous Nitrogen in presence of Sulphites.—Will be inserted in full.

Certain Peculiarities of the Curves of Solubility.—H. Le Chatelier.—A purely mathematical paper.

Property of Discharging Electrised Conductors produced in Gases by the X Rays and by Electric Sparks.—E. Villari.—Gases traversed by the X rays acquire the property of discharging electrised conductors. It results from my most recent researches that they acquire this property rapidly and retain it for some time. In fact, on exciting by the X rays a gas contained in a zinc receiver with a slender wall of aluminium, and propelling it rapidly by a long, thick glass tube (3 × 1000 c.m.) against an electroscope, the latter is seen to be discharged. On the contrary, it is not discharged if the current of gas is not excited by the X rays. The property of discharging conductors is lost by degrees according as the gas passes through longer or shorter tubes, which may be of glass or metal, insulated or not. These experiments have been made with air, oxygen, coal-gas, hydrogen, and a mixture of air and vapours of ether and of carbon disulphide. These gases acquire the same property on passing through a glass tube traversed by a series of induction sparks strengthened by a condenser. The length of the sparks beyond 4 to 5 m.m. has no perceptible influence on this phenomenon. But the efficacy for the discharge is nearly doubled if four sparks are produced in the tube instead of a single one. The induction sparks if not reinforced have an action distinctly weaker, which increases up to a certain limit with the length of the spark and diminishes then down to zero. The efficacy of the reinforced sparks does not decrease if another is produced outside of the tube, but it diminishes distinctly if we augment the resistance of the induced circuit ay means of a column of solution of copper sulphate. The efficiency for the discharge increases a little with the rapidity of the gaseous current and decreases with the length of the tube which conducts the gas to the electroscope. This property cannot be ascribed to a heating produced in the gas by the sparks; on the one hand they heat it only slightly, and on the other hand, if the gaseous column is strongly heated by means of a flame, but not activated by sparks, does not discharge the electroscope.

Succession of the Atomic Weights of Simple Bodies.—M. Delaunay.—This paper will be inserted in full.

Phosphopalladic Ethers, Ammoniacal Derivatives of the Phosphopalladous and Phosphopalladic Ethers.—M. Finck.—An account of phosphopalladic ethyl ether, the corresponding methyl ether, the ammoniacal derivatives of the ethyl and methyl-phosphopalladous ethers, the corresponding palladic ethers, and the action of the compound ammonias upon the ethyl and methyl phosphopalladous ethers, and also that of pyridine upon the same ethers.

The Action of the Electric Effluve on the Property of Gases to discharge Electrised Bodies. —·Emilio Villari.—It results from my former paper that gases acquire the property of discharging electrised bodies not only by the action of the X rays, but also if they are traversed by a series of energetic electric sparks. Further researches enable me to affirm that gases traversed by the sparks seem to acquire a greater conductivity of heat. Two glass tubes, short and thick, connected by other slender tubes, were traversed by one and the same gaseous current. In the first it was possible to produce with platinum wires four sparks furnished by an inductor and reinforced by a condenser; in the second tube there was a small platinum spiral. Through the tubes we drive a gaseous current, and we can, by means of a battery, raise the small spiral to nascent redness; we then activate the tube with sparks; the small spiral cooled and became dark. The experiments were executed with air and coal-gas. The property acquired by gases of discharging electrise bodies might perhaps be ascribed to a kind of dissociation of the gaseous molecules. Guided by this supposition I wished to try the effect of the electric effluve upon gases. By means of an ozoniser I drove upon the electroscope a current of oxygen and of air. I saw that the electroscope was not discharged. It was the same with a current of hydrogen or of coal-gas. The effluve, therefore, does not produce in these gases the power of discharging con-

ductors. But what is particularly remarkable, the effluve seems to destroy in gases the power which they have previously acquired. A gaseous current activated by X rays or by sparks was driven against an electroscope after having passed through a glass ozoniser. With an inactive ozoniser the electroscope was at once discharged, whilst it was no longer discharged on activating the ozoniser. These experiments were performed with air, oxygen, and coal-gas. It is known that the combustion products of flames rapidly discharge conductors. In a recent paper I have shown that this property diminishes a little if the products are cooled by a refrigerating current of water of about 2 metres in length; if we pass these products, hot or cold, tnrongh an ozoniser in activity they lose completely their efficacy for discharging conductors.

## MISCELLANEOUS.

Royal Institution. — A General Monthly Meeting of the Members of the Royal Institution was held Monday afternoon (the 2nd inst.), Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—Mr. George Cawston, Mr. J. Broughton Dugdale, J.P., D.L., Mr. Henry Harben, J.P., and Mr. John H. Usmar. The special thanks of the Members were returned to the Proprietors of the *Times*, Dr. Ludwig Mond, F.R.S., Prof. Dewar, and Sir Andrew Noble, for their donations to the fund for the promotion of Experimental Research at Low Temperatures. It was also announced that the Christmas Lectures specially adapted for children will this year be given by Prof. Silvanus P. Thompson, F.R.S., his subject being " Visbile and Invisible Light "; and it was reported that the Managers had elected Prof. Augustus D. Waller, M.D., F.R.S., Fullerian Professor of Physiology for three years, the appointment to date from January 13th, 1897, and also that the managers had appointed Dr. Alexander Scott, M.A., D.Sc., to be Superintendent of the Davy Faraday Research Laboratory of the Royal Institution, the Directors already appointed by the Managers being Lord Rayleigh and Professor Dewar. After the Meeting the Members inspected the new rooms which have been lately added to the Library of the Royal Institution, through the munificence of Dr. Ludwig Mond, F.R.S., which rooms will provide increased accommodation for the Members on the occasion of the Friday Evening Meetings.

# THE CHEMICAL NEWS.

## ACTION OF METALS AND THEIR SALTS ON THE ORDINARY AND ON THE RÖNTGEN RAYS—A CONTRAST.*

By J. H. GLADSTONE, F.R.S., and W. HIBBERT.

THIS paper, which was communicated to Section B of the British Association at Liverpool last September, was a preliminary notice of an investigation that is still on hand. It is an extension in a new direction of previous work on the optical properties of metals and salts, the results of which have been published from time to time during the last thirty-nine years. The present experiments were made in Mr. Hibbert's laboratory in the Polytechnic, Regent Street, London, the method adopted being very similar to that generally employed for X ray work. The paper was accompanied by numerous photographs, most of which included a scale made of different thicknesses of aluminium.

### I. *Action of Metals on the Ordinary Rays.*

It is well known that metals in the solid condition absorb ordinary light completely, though very thin plates of silver and gold transmit certain rays to a small extent. It is, however, a remarkable fact that when these metals combine with an acid radical, they cease to absorb ordinary light. This is quite true in regard to the metals of the alkalies, of the alkaline earths, and of the earths, as well as in regard to most of the ordinary metals. There are two groups of metals of which the remark cannot strictly be made, for they exhibit the absorption of certain rays, while others are transmitted. These are the great iron group, and the group that includes gold and most of the noble metals; all of these are to be found in the eighth column of Mendeleeff's table, or near it. There is, we believe, no soluble metallic salt known which is absolutely opaque.

The solutions of the colourless salts are themselves colourless when the solvent is colourless. The solutions of the coloured salts are generally, but not always, of the same colour as the undissolved salt.

### II. *Action of Metals on the Röntgen Rays.*

The action on these rays exhibits a great contrast. All the metals, as far as they have been examined, instead of wholly absorbing, transmit the Röntgen rays more or less. This was one of the earliest observations of Röntgen, and it has been confirmed by many other observers. We have extended the list to the alkaline metals, and find that lithium (the metal of lowest density) is almost absolutely transparent; and there is every gradation between it and the noble metals, which are practically opaque, the slightly transparent gold being amongst the most opaque for X rays.

When the metals combine with acid radicals, they exhibit the same, or nearly the same, absorption as they do when in the uncombined condition. Thus, in a score of instances, we have found that the formates and acetates of lithium, potassium, sodium, calcium, zinc, aluminium, and lead, showed an absorption analogous to that of the metals themselves, and we have met with no marked exception. This is absolutely different from what occurs in the case of the ordinary rays.

In the few instances we have yet tried, the solution of a salt in water has the same action on the Röntgen rays

as the salt itself. The best instance is that of formate of potassium, which dissolves in so little water that the effect of the solvent is negligible.

### III.—*The Order of Absorption.*

The order of absorption of the X rays by metals was at first supposed to be the same as that of their density. We find, however, with the alkali metals, that the order of absorption is lithium, sodium, potassium, while that of their density is lithium, potassium, sodium.

It has been shown by Prof. Barrett (*Proceedings Royal Dublin Society*, May, 1896) and others that the absorption follows the order of the atomic weights rather than that of the density.

From certain experiments which we have recently made on the refraction of metals, we were especially interested in observing whether the order was that of the atomic weights, or that of the equivalents. It was tested in the case of potassium and calcium, which have practically the same atomic weights—39 and 40—though their equivalents differ, being 39 and 20. It was found that whether tested by the uncombined metals or by their salts, the absorptions of the Röntgen rays by the two metals are about the same for thicknesses answering to the atomic weights, while they are very different for thicknesses answering to the combining proportions. The three metals, sodium, magnesium, and aluminium (atomic weights 23, 24, 27; combining weights 23, 12, 9, respectively) showed the same thing, though not so clearly. Mercury was found to give practically the same amount of absorption in the mercurous and mercuric acetates.

In dealing with metals, whether uncombined or in salts, the order of their absorption for these rays is, in fact, that of their atomic weight, but the amount of absorption increases much more rapidly than the atomic weights themselves.*

In attempting to estimate the absorbent value of the different metals from their salts, we were led to prefer the formates, as the acid radical ($CHO_2$) has a low equivalent and has scarcely any absorbent effect. Where the formate was not available we adopted the acetate. Similarly, as lithium has next to no absorbent action on the Röntgen rays, its salts afford the best means of determining the effect of the different acid radicles.

The general law to which our experiments tend is, that the absorption of a dry salt, whether crystallised or not, is an additive property, the sum of the absorptions of its two constituents. The absorption of a solution is apparently that of the salt itself, plus that of the solvent.

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## ON METHODS OF DETERMINING THE DRYNESS OF SATURATED STEAM, AND THE CONDITION OF STEAM GAS.†

By Prof. OSBORNE REYNOLDS, M.A., LL.D , F.R.S.

(ABSTRACT).

IN certain recent attempts to ascertain the proportion of steam and water in the fluid which enters a steam-engine, by means of what is called the wire-drawing calorimeter, the published results show that there remains from 0 to 5 per cent by weight of water in the steam, after it has been drained by gravitation, in the same manner as the steam on which Regnault's experiments were made. This has necessarily excited great interest and is naturally welcome, as it apparently brings the per-

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* Read before the British Association (Section B), Liverpool Meeting, 1896.

* The order of progression in the absorption of different salts has been to a certain extent worked out previously by Novák and Sulc, *Zeit. Ph. Ch.*, February, 1896; and by Blennard and Labesse, *Comptes Rendus*, March, 1896. See also remarks made by Prof. Dewar at the Royal Society, as reported in the *Times* of February 15.
† Read before the Manchester Literary and Philosophical Society, November 3, 1896.

formance of the engines by so much nearer perfection. Although the results of these recent experiments appear to show the condition of dry saturated steam to be other than that on which Regnault's experiments were made, and from which the present steam tables have been calculated, still these tables have been used in deducing the percentage of water latent in the steam. Whereas, if the latent water exists, it must have existed in the steam used by Regnault, and the steam tables must also be subject to identical corrections; and, consequently, the percentage of theoretical performance of steam engines would be unchanged.

It is then pointed out that, in the reduction of such of these results as have been published, use has been made of Regnault's determination of the specific heat at constant pressure of steam gas (0·48) in a manner which is not consistent with the theory of thermodynamics. Thus, in Rankine's notation, $S_I$ is the weight of steam per lb. of fluid, and $H_I$ the total heat per lb. from $0°$ C. to $T_I°$, $h_I$ the heat required to raise water per lb., and $H_2$, $h_2$, $T_2$, the corresponding values for saturated steam at the pressure after wire-drawing, and $T_s°$ the observed temperature after wire-drawing.

The notation assumed for the equation of heat, neglecting incidental losses, is—

$$S_I (H_I - h_I) + h_I = H_2 + 0·48 (T_s° - T_2°) \dots \text{I.}$$

Whereas, it has been proved by Rankine that the thermodynamic expression for the total heat in superheated steam at $T_s°$ C., provided it has reached the condition of steam gas, to which the 0·48 only applies, is—

$$C_I + 0·48 (T_s° - T_0°).$$

$C_I$, being a constant, depends only on the temperature of the water ($T_0°$) from which the steam is produced, the value of which from $0°$ C. is 606·7, approximately, as deduced by Rankine.

Using Regnault's formula for $H_2$, the right member of equation (1) becomes—

$$606·5 + 0·305 T_2° + 0·48 (T_s° - T_2°),$$

while the value by the thermodynamic formula is—

$$606·7 + 0·48 T_s°,$$

which gives as the excess of heat over that assumed—

$$0·2 + 0·175 T_2°.$$

This excess, if $T_2$ were $100°$ C, is 17·7 thermal units, and if the initial steam pressure were 200 lbs. above the atmosphere, the latent heat being 467·5 thermal units, the percentage of water it would evaporate at boiling-point is—

$$\frac{177}{467·5} = 3·8 \%,$$

which is about as much as needs to be accounted for.

It is also shown that, in order to render Rankine's formula applicable to wire-drawing experiments, it is necessary that the wire-drawing should be continued till the steam is gaseous, whence arises the difficulty of securing that this state has been reached. This, however, may be secured by lowering the pressure gradually after wire-drawing, and so increasing the extent of wire-drawing while observing the temperature ($T_s°$), which, after falling, will gradually become constant as the wire-drawing increses, and, when constant, will be a definite indication of this gaseous state.

The necessary conditions to ensuring accuracy are then considered. and, in conclusion, it is stated that a research to verify these conclusions has been commenced by Mr. J. H. Grindley, B.Sc., in the Engineering Laboratory of Owens College, Manchester.

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**The Iodine Number of Cocoa Butter.** — Dr. F. Filsinger.—The author has made comparative experiments on kauka beans, kauka-mass, and kauka chocolate. The highest iodine number found was 37·5 in a sample from Sumana, and the lowest, 33·5, was yielded by that from Machala-Guayaquil.

## A NEW BLUE DYE OBTAINED FROM QUINONE.

By Dr. JAMES LEICESTER, F.C.S.,
Lecturer on Chemistry and Metallurgy at the Merchant Venturers' Technical College, Bristol.

WHEN benzoquinone, $C_6H_4O_2$, is heated in glacial acetic acid solution with O nitroaniline, $C_6H_4(NO_2).NH_2$, a substance called dinitrodianilidoquinone is formed, having the following composition :—
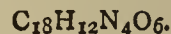
$$C_{18}H_{12}N_4O_6.$$

0·1360 grm. of the substance yielded 0·2860 grm. of carbon dioxide and 0·0380 grm. of water.
0·1420 grm. of the substance yielded 18 c.m. of nitrogen at $21°$ C. and under a pressure of 741 m.m.
Taking $C_{18}H_{12}N_4O_6$ as the formula—

|   |   |   |   |   |   | Found by analysis. |
|---|---|---|---|---|---|---|
| C | .. | .. | .. | .. | 56·84 | 57·35 |
| H | .. | .. | .. | .. | 3·15 | 3·10 |
| N | .. | .. | .. | .. | 14·73 | 14·84 |

These results would give the following graphic formula :—
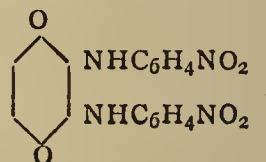


It can be easily crystallised from absolute alcohol. When pure it melts at $305°$ C.

If the dinitrodianilidoquinone, $C_{18}H_{12}N_4O_6$, be reduced by means of alcoholic ammonium sulphide, a dark green coloured powder is obtained which dissolves in acetic acid with an intense blue colour; the solution readily dyeing silk and woollen goods. The colour is a fast one, not fading with the action of sunlight, or coming out on washing. If dilute sulphuric acid be added in small quantities to the acetic acid solution a very strong fluorescence is obtained.

Light passing through the solution has a rich blue colour; the light reflected from the solution being a deep red in colour.

An analysis of the substance gives the following results.

$$C_{18}H_{10}N_4O_2.$$
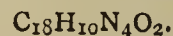
|   |   |   |   |   | Theory. | Found. |
|---|---|---|---|---|---|---|
| C | .. | .. | .. | .. | 68·7 | 68·5 |
| H | .. | .. | .. | .. | 2·3 | 3·9 |
| O | .. | .. | .. | .. | — | — |
| N | .. | .. | .. | .. | 17·8 | 17·7 |

The following formula represents its probable constitution :—
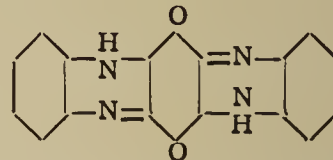


A cheaper process is necessary for the manufacture of the dye, which is known commercially as Istarine.

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**City and Guilds of London Institute.** — The following is a list of Scholarships awarded in connection with the present Session, 1896-97, of this College :— Clothworkers' Scholarship (£60 a year, with free education for two years), L. P. Wilson ; Mitchell Scholarship (£40 a year, with free education for two years), R. S. Potter; Clothworkers' Technical Scholarship (£30 a year, with free education for two years), E, W. Cook ; David Salomons Scholarship (£50), E. W. Marchant ; John Samuel Scholarship (£30), H. W. Hanbury ; Institute's Scholarships (free education for three years), F, S, Miller, J. I. Hunter, F. W. Fawdry.

# ON THE INVERSION OF SUGAR BY SALTS.*
## No. II.
### By J. H. LONG.
(Continued from p. 232).

## Manganous Chloride.

THE salt used was purified by several crystallisations from the best obtainable Schuchardt product.

### Experiment 14.

$MnCl_2.4H_2O.$   N/4.
In 250 c.c., 50 grms. of sugar $+$ 6·18 grms. of chloride.
A = 35·00.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 26·70° | — | — | — |
| 15 | 26·60 | 0·10° | 0·00124 | 0·00009 |
| 45 | 26·30 | 0·40 | 0·00499 | 0·00011 |
| 75 | 26·00 | 0·70 | 0·00878 | 0·00012 |
| 135 | 25·25 | 1·45 | 0·01838 | 0·00014 |
| 255 | 22·66 | 4·04 | 0·05327 | 0·00021 |
| 375 | 18·75 | 7·95 | 0·11190 | 0·00030 |

The high initial rotation here is very extraordinary, corresponding to a specific rotation of 66·75°.

### Experiment 15.

$MnCl_2.4H_2O.$   N/2.
In 250 c.c., 50 grms. of sugar$+$12·35 grms. of chloride.
A = 34·84.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 26·54° | — | — | — |
| 15 | 26·45 | 0·09° | 0·00113 | 0·00008 |
| 45 | 26·16 | 0·38 | 0·00476 | 0·00011 |
| 75 | 25·85 | 0·69 | 0·00869 | 0·00012 |
| 135 | 24·52 | 2·02 | 0·02594 | 0·00019 |
| 255 | 22·26 | 4·28 | 0·05693 | 0·00022 |
| 375 | 17·15 | 9·39 | 0·13639 | 0·00036 |
| 495 | 13·00 | 13·54 | 0·21370 | 0·00043 |
| 555 | 11·52 | 15·02 | 0·24498 | 0·00044 |

### Experiment 16.

$MnCl_2.4H_2O.$   N.
In 250 c.c., 50 grms. of sugar$+$24·70 grms. of chloride.
A = 34·63.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 26·33° | — | — | — |
| 15 | 26·12 | 0·21° | 0·00264 | 0·00018 |
| 30 | 25·86 | 0·47 | 0·00593 | 0·00020 |
| 60 | 25·15 | 1·18 | 0·01505 | 0·00055 |
| 120 | 23·05 | 3·28 | 0·04321 | 0·00036 |
| 180 | 20·07 | 6·26 | 0·08659 | 0·00048 |
| 300 | 15·60 | 10·73 | 0·16105 | 0·00054 |

### Experiment 17.

$MnCl_2.4H_2O.$   2N.
In 250 c.c., 50 grms. of sugar$+$49·40 grms. of chloride.
A = 34·18.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 25·88° | — | — | — |
| 15 | 25·38 | 0·50° | 0·00640 | 0·00043 |
| 45 | 23·91 | 1·97 | 0·02578 | 0·00057 |
| 75 | 22·21 | 3·67 | 0·04933 | 0·00065 |
| 135 | 18·25 | 7·63 | 0·10971 | 0·00081 |
| 195 | 14·80 | 11·08 | 0·17016 | 0·00087 |
| 345 | 5·25 | 20·63 | 0·40183 | 0·00116 |

No very plain relation can be found connecting these rates of inversion. The coefficients corresponding to the time of completion of one-third of the inversion are here given.

| Conc. | K. |
|---|---|
| 1 | (0·00038) |
| 2 | 0·00041 |
| 4 | 0·00055 |
| 8 | 0·00088 |

The first coefficient had to be estimated and is uncertain.

## Ferrous Chloride.

Considerable difficulty was experienced in preparing a solution of ferrous chloride devoid of traces of free acid. A weighed excess of pure iron wire was covered with water in a small flask, and then the calculated volume of titrated hydrochloric acid was added in amount just sufficient to produce the solution of required strength. The mixture was gently warmed and allowed to stand a short time. Warming was repeated at intervals through several hours, until the liberation of hydrogen became very feeble. The solution so obtained stood five days in the presence of the excess of iron, being boiled twice in the interval, and was then filtered cold into the sugar solution, which was made up to the proper volume with fresh distilled water.

The actual strength of solutions made in this manner was determined by titration later. The two following were almost exactly normal and half-normal.

Both solutions became turbid on heating and had to be filtered before polarisation for the first tests. After the lapse of about two hours the cloudiness disappeared, and the solutions then taken from the thermostat were clear enough for direct polarisation.

### Experiment 18.

$FeCl_2.$   N/2.
In 250 c.c., 50 grms. of sugar $+$ 7·925 grms. of chloride.
A = 16·18.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 12·03° | — | — | — |
| 15 | 9·47 | 2·56° | 0·07507 | 0·00500 |
| 45 | 7·44 | 4·59 | 0·14517 | 0·00322 |
| 105 | 5·00 | 7·03 | 0·24783 | 0·00236 |
| 165 | 3·83 | 8·20 | 0·30725 | 0·00186 |
| 285 | 1·90 | 10·13 | 0·42749 | 0·00150 |
| 405 | −0·50 | 12·53 | 0·64696 | 0·00160 |
| 525 | −2·01 | 14·04 | 0·87884 | 0·00167 |

### Experiment 19.

$FeCl_2.$   N.
In 250 c.c., 50 grms. of sugar$+$15·85 grms. of chloride.
A = 15·71.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 11·56° | — | — | — |
| 15 | 9·40 | 2·16° | 0·06424 | 0·00428 |
| 45 | 6·88 | 4·68 | 0·15360 | 0·00341 |
| 105 | 4·75 | 6·81 | 0·24679 | 0·00235 |
| 165 | 3·56 | 8·00 | 0·30913 | 0·00188 |
| 285 | 1·15 | 10·41 | 0·47190 | 0·00165 |
| 405 | −1·42 | 12·98 | 0·76002 | 0·00187 |
| 525 | −3·25 | 14·81 | 1·24194 | 0·00236 |

These results are very surprising, inasmuch as they show but little difference between the rates for the two concentrations. In both instances the rates rapidly decrease from the beginning, and after the sugar has been about half inverted they increase a little. I give next some results from solutions which had not been boiled so thoroughly, and which may have held a little free acid.

### Experiment 20.

$FeCl_2.$   0·52 N.
In 250 c.c., 50 grms. of sugar$+$8·242 grms. of chloride.
A = 34·00.

| $t$. | $a$. | $x$. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 25·70° | — | — | — |
| 15 | 20·00 | 5·70° | 0·07969 | 0·00531 |
| 45 | 12·80 | 12·90 | 0·20720 | 0·00460 |
| 75 | 9·00 | 16·70 | 0·29343 | 0·00391 |
| 105 | 6·19 | 19·51 | 0·37041 | 0·00353 |
| 165 | 2·42 | 23·28 | 0·50129 | 0·00304 |
| 285 | −1·95 | 27·65 | 0·72771 | 0·00256 |
| 345 | −3·96 | 29·66 | 0·89399 | 0·00258 |
| 405 | −5·30 | 31·00 | 0·05436 | 0·00260 |

*Experiment 21.*

$FeCl_2$. 0·98 N.

In 250 c.c., 50 grms. of sugar + 15·53 grms. of chloride.
A = 33·60.

| t. | a. | x. | Log. $\frac{A}{A-x}$. | $\frac{1}{t}$ log. $\frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 25·30° | — | — | — |
| 15 | 19·84 | 5·46° | 0·07702 | 0·00513 |
| 45 | 14·20 | 11·10 | 0·17416 | 0·00387 |
| 75 | 11·80 | 13·50 | 0·22314 | 0·00297 |
| 105 | 9·88 | 15·42 | 0·26675 | 0·00254 |
| 165 | 7·65 | 17·65 | 0·32358 | 0·00196 |
| 285 | 1·45 | 23·85 | 0·53734 | 0·00188 |
| 345 | − 1·50 | 26·80 | 0·69383 | 0·00201 |

The effect of free acid is not apparent. Six other experiments were made with normal and half-normal ferrous chloride solutions, the results of which were very similar to those above. In all cases the constant was found to increase before the completion of the inversion.

The constant for 0·001 N hydrochloric acid was determined for comparison at the same temperature, $t = 85°$, and with the same amount of sugar. It was found—

$$K = 0·0051.$$

(To be continued).

## THE NEW ELEMENTS OF CLEVEITE GAS.

### By J. R. RYDBERG.

THE excellent investigations of Runge and Paschen on the spectrum of cleveite gas (*Astrophysical Journal*, iii., 4—28, 1896) have made the existence of another new element besides helium very probable.* But the method of forming the spectral series seems to rest upon rather an insecure basis, although by the help of the relation between the principal series and the sharp series (second subordinate series of Kayser and Runge), which I long ago pointed out, it would have been very easy to state clearly the true connection. The relation in question, which comprehends the above-mentioned series in a single common formula, is derived from the observation that the first term of a principal series forms at the same time the first term of the corresponding sharp series, or, to state the same thing in another form,—

*The difference between the common limit of the nebulous and the sharp series and the limit of the corresponding principal series gives the wave-number† of the common first term of the sharp and the principal series.*

If we designate the limits of the series by $D$ (nebulous), $S$ (sharp), $P$ (principal series), the order of the series by subscripts to the symbols of the elements (stronger series 1, weaker 2), and the mean of $D$ and $S$ by $M$, we have for the alkali metals:—

| | D | S | M | P |
|---|---|---|---|---|
| Li | 28582·92 | 28582·16 | 28582·54 | 43482·53 |
| $Na_1$ | 24468·89 | 24471·36 | 24470·13 | 41452·61 |
| $Na_2$ | 24486·08 | 24488·55 | 24487·32 | 41452·61 |
| $K_1$ | 21959·52 | 21951·39 | 21955·46 | 35008·92 |
| $K_2$ | 22017·37 | 22009·24 | 22013·31 | 35008·92 |
| $Rb_1$ | 20861·25 | 20877·05 | 20869·15 | 33706·66 |
| $Rb_2$ | 21098·83 | — | 21098·83 | 33705·59 |

Hence, if we call $P_1$ the first term of a principal series, we have—

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* For the new elements I use the symbols A (Argon), He (Helium), Pa (Parhelium).

† By *wave-number* I mean the number of waves in 1 c.m. See *Svenska Vetensk. Akad. Handl.*, xxiii., 35, 1890.

| | P—M | $P_1$ | Diff. |
|---|---|---|---|
| Li | 14899·99 | 14903·03 | − 3·04 |
| $Na_1$ | 16982·48 | 16972·70 | + 9·78 |
| $Na_2$ | 16965·29 | 16955·51 | + 9·78 |
| $K_1$ | 13053·46 | 13041·72 | +11·74 |
| K | 12995·61 | 12984·63 | +10·98 |
| $Rb_1$ | 12837·51 | 12798·95 | +38·56 |
| $Rb_2$ | 12606·76 | 12575·18 | +31·58 |

For Pa and He, on calculating the limits by the same method which I have used for the other elements, I have found the following values:—

| | D | S | M | P |
|---|---|---|---|---|
| Pa | 27174·47 | 27175·00 | 27174·74 | 32032·53 |
| He | 29222·70 | 29222·63 | 29222·67 | 38452·89 |

where the connection of the series is still undecided. By using the above-mentioned relation in the calculation of the values of $P_1$, two combinations present themselves, viz.,—

| | P | M | P—M | P obs. | Diff. | Mean error. |
|---|---|---|---|---|---|---|
| Pa | 32032·53 | 27174·74 | 4857·79 | 4900·65 | − 42·86 | 20 |
| He | 38452·89 | 29222·67 | 9230·22 | 8950·14 | +280·08 | 40 |

and—

| | P | M | P—M | P obs. | Diff. | Mean error. |
|---|---|---|---|---|---|---|
| Pa | 38452·89 | 27174·74 | 11278·15 | — | — | — |
| He | 32032·53 | 29222·67 | 2809·86 | — | — | — |

Although the calculated values of $P_1$ differ very considerably from the observed values, there can be no doubt that the first combination, which is the one chosen by Runge and Paschen, is the only possible one, for the lines calculated from the second were not observed. We meet here with the not very common case in which the calculated values greatly surpass the observations in accuracy, the limits of error for the values of $M$ and $P$ amounting at most to one unit, while the mean errors of the two values of $P_1$, determined with the bolometer, are 20 and 40 respectively. The differences found certainly exceed the errors to be expected, but the analogy with the spectra of the alkali-metals speaks so decisively in favour of an exact agreement between the values of $P_1$ and $P—M$, that I do not hesitate to ascribe the differences to errors of observation.

In order to judge better of the possibility of such differences I have examined the observations of Runge and Paschen, first reducing to wave-lengths the extreme values of the angular determinations (Runge and Paschen, p. 27). Thus we find:—

| Observed maximum. | Observed minimum. | Mean. | Calculated value. |
|---|---|---|---|
| 21040 | 19500 | 20400 | 20580·0 |
| 11450 | 10540 | 11170 | 10831·0 |

whence it appears that the calculated values lie within the limits of the observations. A closer examination shows that the angular determinations group themselves about well-defined means, by no means symmetrically, but so that the greater values are much more numerous than the smaller ones, and at the same time more distant from the closely concentrated central groups. At the line 11170 we even find two distinct groups. The distribution of the values is shown in the following table.

| Wave-length according to R. and P. | No. of values of central group. | Range in angular values of central group. | Mean wave-length of central group. | No. of greater values. | No. of smaller values. | Diff. from mean of greatest value. | Diff. from mean of smallest value. |
|---|---|---|---|---|---|---|---|
| 20400 | 7 | 0′·10 | 20580 | 12 | 3 | 2′·63 | 1′·17 |
| $11170_1$ | 7 | 0′·15 | 11350 | 5 | 1 | 2′·32 | 0′·28 |
| $11170_2$ | 9 | 0′·18 | 11190 | 4 | 2 | 1′·87 | 0′·73 |
| 7280 | 7 | 0′·10 | 7330 | 7 | 3 | 2′·82 | 0′·48 |

The greater deviation of the larger values seems to indicate a broadening of the lines in the direction of the

shorter wave-lengths. But, however this may be, the arithmetical mean of the observations under these circumstances gives by no means the most probable value of the quantity in question. I have therefore calculated the mean angular values of the central groups, and with the aid of the table (*loc. cit.*, p. 25) deduced the mean wave-lengths. For the first line the value thus obtained coincides exactly with the number calculated above ; this, however, must be regarded as partly accidental. The third line does not agree as well as before, but still falls within the limits of the errors of observation. As to the second line, the doubling of the central group agrees perfectly with an hypothesis which had suggested itself previously and quite independently to explain the considerable discrepancy between observation and calculation. According to Runge and Paschen the strong Na lines in the visible and ultra-violet spectrum come out with great intensity; it could therefore scarcely be doubted that the line 11392·5 in the infra-red would also appear. It was also to be expected that in the bolometric determinations this line would form with the adjacent 10831·0 a single thermal maximum, and retain only a feeble indication of its double origin; the two thermal maxima, if they are still to be discerned as separate lines, ought at all events to appear very close together on account of the superposition.

But this is just what we have found, for according to Runge and Paschen the general mean of the wave-length determinations gives the value 11170, which would come out as the mean of the two wave-lengths mentioned above, if the intensity of the Na line were 1·5 times as great as that of the He line. The two values which I have calculated from the central groups of the observations would indicate a sharp Na line and a broad He line. The determinations do not, however, allow any perfectly definite conclusions to be drawn. But I believe that the preceding considerations will suffice to prove the importance of making further measures of the two infra-red lines. The accuracy attained by Lewis in his bolometric measurements (Lewis, *Astrophysical Journal*, ii., 1—25, 1895) would be quite sufficient to decide the present question. At all events I do not doubt that the calculated values 4858 and 9230 will be found for the wave-numbers of the lines *in vacuo*.

In this connection I cannot refrain from mentioning that the two new elements of clèveite gas, as well as argon, seem to be subject to a regularity regarding their atomic weights, to which I called attention some years ago (*Svenska Vetensk. Acad. Handl.*, xi., No. 13, 1886). The rule in question may be expressed as follows :—

*If the atomic weights of the elements, which form the first rows of the periodic system, be reduced to the nearest integral numbers, the elements of uneven valency will have the form $4n-1$, and the elements of even valency the form $4n$.*

On account of the uncertainty of the determinations of atomic weights and their increasing differences from integral numbers, the rule could be traced with some certainty only for the first twenty-two elements (to Fe inclusive). It shows here three exceptions, viz., Be (9 instead of 8), N (14 instead of 15), and Sc (44 instead of 43), but it gives place for He (4) and A (20), as well as for an element with the atomic weight 3, which would possibly answer to Pa. Spaces remain for elements with the reduced atomic weights 36, 44, and 47. The series of numbers is shown in the table which follows.

Of the six places formerly vacant in the present division two are probably permanently taken up by the new elements He and A. According to analogy these elements should have an even valency, while Pa might possess an atomic weight 3 and an uneven valency. For further particulars, as well as for regularities which appear on advancing further in the series of elements, I will refer to the paper mentioned above. It seems not quite impossible that the present exceptions may yet submit to the rule, when we consider the imperfection of our knowledge of the metals of the so-called rare earths (Be and Sc) and keep in view the surprising discoveries of the impurities of nitrogen.

| $n$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Element | Pa | Li | B | N | Fl | Na | Al |
| P | ? | 7·01 | 10·9 | 14·01 | 19·06 | 22·995 | 27·04 |
| $4n-1$ | 3 | 7 | 11 | (15) | 19 | 23 | 27 |
| Element | He | Be | C | O | A | Mg | Li |
| P | 4·0 | 9·03 | 11·97 | 15·96 | 19·94 | 24·3 | 28·3 |
| $4n$ | 4 | (8) | 12 | 16 | 20 | 24 | 28 |

| $n$ | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|
| Element | P | Cl | K | Sc | — | V | Mn |
| P | 30·96 | 35·37 | 39·03 | 43·97 | — | 51·1 | 54·8 |
| $4n-1$ | 31 | 35 | 39 | (43) | 47 | 51 | 55 |
| Element | S | — | Ca | — | Ti | Cr | Fe |
| P | 31·98 | — | 39·91 | — | 48·0 | 52·0 | 55·88 |
| $4n$ | 32 | 36 | 40 | 44 | 48 | 52 | 56 |

It is hardly possible that the approximation of the atomic weights to integral numbers, the correspondence in the number of elements in the two series of different valencies, and in the simultaneous evenness and unevenness of the integral numbers and the valencies, can be a mere chance.

The vacant places which still exist between Sc and Ti, as well as between the corresponding terms of the following periods, seem only to add further support to the rule proposed, inasmuch as they afford very necessary space for the numerous metals of the rare earths.— *Astrophysical Journal*, iv., No. 2, August, 1806.

## TETRA-NITRO-CELLULOSE: A NEW EXPLOSIVE.

By H. N. WARREN, Principal Liverpool Research Laboratory.

WHEN dinitro-cellulose, or ordinary soluble pyroxylin, is further acted upon by means of a mixture composed of equal parts by volume of nitric acid 1·5 density, and concentrated sulphuric acid, there is, as is well known, produced a true trinitro compound, differing entirely from either of the above compounds as regards its solubility, and at the same time possessing far enhanced explosive properties.

If the resulting compound thus formed is again treated with a still more energetic dehydrating agent, composed of equal parts by weight of commercial vitriol and phosphoric anhydride, a further nitrogenous compound is obtained, which, after the usual washing and drying, presents a much more brittle structure than any of the preceding derivatives, in some cases even admitting of pulverisation, and altogether a much more formidable compound, even exploding by mere percussion, its explosive violence as compared with the former bodies being more than double.

When the compound is digested in a strong solution of potassium chlorate, and carefully dried, it is rendered extremely brittle, and thus readily admits of being pulverised, forming a true percussion agent. As far as can at present be ascertained the new explosive represents a tetra-nitro compound ; but owing to its formidable explosive properties, necessitating considerable care in handling the same, further investigations are considered necessary, in order to arrive at a correct formula. The compound, when submitted to destructive distillation, in contact with moist caustic potash, evolves hydrogen gas, together with large quantities of methylic alcohol.

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## SOME COLOUR REACTIONS OF BRUCINE; DETECTION OF NITROUS NITROGEN IN PRESENCE OF SULPHITES.

### By P. PICHARD.

IN our studies on the oxidising action of plaster in contact with nitrogenous organic matters we have been led to search for the existence of nitrous nitrogen in presence of oxygenous compounds of sulphur, sulphites, and hyposulphites, as well as alkaline and alkaline earthy sulphides. The most sensitive procedures for the detection of nitrous nitrogen are those of Griess, Tromsdorff, and Piccini. We have found that the colouration of brucine by hydrochloric acid on contact with a nitrite yields a reaction similar in sensitiveness to these procedures, and greater in presence of sulphites and hyposulphites.

A drop of solution of a nitrite mixed upon a porcelain plate with a drop of pure hydrochloric acid gives, with a particle of brucine, in at most 5 minutes a colouration which passes from vermilion to light yellow. We may thus detect one part of nitrous nitrogen in 640,000 parts of water. Hydrochloric acid under the same conditions gives nothing with a nitrate.

Chlorine and the hypochlorites do not colour brucine, but they give instantly an intense vermilion in the solutions of certain salts of brucine, the nitrate, the hydrochlorate, acetate, and sulphate. The sulphuric solution of brucine is the most rapidly and strongly coloured, as this acid more than others favours the formation of a yellow nitrated alkali, cacotheline, the ultimate result of oxidation.

The presence of a sulphite much diminishes the sensitiveness of the procedures of Piccini, Tromsdorff, and Griess for the detection of nitrous nitrogen.

Piccini's method is inapplicable in this case; traces of ferrous sulphite give in a dilute solution of ferrous sulphate, to which a little acetic has been added, the brown colour which shows the presence of nitrous nitrogen.

*Tromsdorff's Method.* — The proportion of 1/600 of $SO_2$ in the liquid reduces the sensitiveness of the reaction from 1/1,000,000 to 1/30,000; for 1/1800 of $SO_2$ the sensitiveness is 1/57,500.

*Method of Griess.* — 1/2040 of $SO_2$ reduces the sensitiveness from 1/100,000,000 to 1/65,200; the sensitiveness is become more than 1000 times less.

*Method with Brucine and Hydrochloric Acid.* — 1/2000 of $SO_2$ reduces the sensitiveness from 1/640,000 to 1/329,000, or only one-half.

In consequence of the direct addition of gypsum to soils, and the use of superphosphates in manures, the alkaline and alkaline earthy sulphides, sulphites, and hyposulphites may be found in notable quantity in drain waters, or the lixivium of a soil or a compost. If we wish to search for nitrous nitrogen in such waters we must first prove the presence or the absence of sulphides and sulphites. The sulphides are detected by lead acetate, silver acetate, or sodium nitro-prusside. We have satisfied ourselves that they do not affect the colour reaction of brucine.

Among the reactions indicated for the detection of sulphurous acid we do not know any for the present case in presence of a nitrite more distinct and more sensitive than the odour of this acid when it escapes into the air.

The liberation of sulphurous acid by the action of a strong acid, cold or hot, being accompanied by an escape of hydrogen sulphide (if the liquid contains a sulphide), and the odour of hydrogen sulphide being able to mask that of $SO_2$, it is necessary in this case to eliminate the greater part of the hydrogen sulphide. This is easily affected by agitating the liquid with lead sulphate in fine powder. We decant, filter the liquid, and then treat it in a test-tube with a few drops of sulphuric acid, at first in the cold and then at ebullition. Traces of $SO_2$ may be detected in this manner.

If there is no sulphurous acid, we search for and determine nitrous nitrogen by the procedures of Tromsdorff or Griess.

If we have recognised the presence of a sulphite after having tested the liquid by the two methods above given without positive result, we have recourse to the use of brucine and hydrochloric acid, which will permit us to recognise 1/329,000 of nitrogen in presence of 1/2060 of $SO_2$, and consequently to affirm the existence of nitrous nitrogen when the other methods fail to detect it.

The method of operation is that which we have given for the detection and determination of nitric acid by the aid of brucine and sulphuric acid.

The drainage water or the liquid derived from the lixiviation of a soil or a compost must be clarified and decolourised by filtration over finely washed animal charcoal.

The lixiviation must be effected with the smallest possible quantity of water, at most ten parts of water to one part of material. The mixture is rapidly raised to ebullition in a flask, which is then stoppered and shaken from time to time until completely cold. The liquid is then filtered over animal charcoal. From the filtrate we take a drop and place it upon a porcelain plate, and mix with it a drop of pure hydrochloric acid quite free from chlorine and nitrous products, and of sp. gr. 1'21. We spread it with a platinum wire so as to cover a surface of the size of a half-franc. We let fall into the middle of the liquid a fragment of brucine of the size of a pin-head. We wait five minutes at most until the appearance of a tint varying from vermilion to light yellow. If no colour appears we cannot affirm the presence of nitrous nitrogen.

The determination of small quantities of nitrous nitrogen, founded on the comparison of tints or the disappearance of these tints on dilution, is very uncertain in presence of alkaline or alkaline-earthy sulphites or hyposulphites.

We may correct the results obtained and render them more exact by determining the proportion of $SO_3$ contained in a part of the liquid.—*Comptes Rendus,* cxxiii., 590.

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## THE PRESENCE OF NITRITES IN THE AIR.[*]

### By GEORGE DEFREN, M.S.

(Concluded from p. 231).

THE investigation next carried out was to make a quantitative estimation of the nitrites by volume, by a method similar to that usually made use of in determining the quantity of carbon dioxide in the air of buildings. Two large bottles, the capacities of which were known, were placed side by side, and the air to be analysed was drawn into them, using suction, one tube reaching nearly to the bottom of the bottle. They were then tightly closed with rubber stoppers, and taken to the room where they were to be tested. 100 c.c. best re-distilled water, free from nitrites, were then introduced, the bottles allowed to stand, with occasional shaking, for more than twelve hours—in some cases for as many as twenty-four hours—before analysis. The water was then tested for nitrites in the usual manner.

Two samples of air from Room 36 were taken at 3'30 p.m. Fifteen lamps had been in use for about two hours. Three persons were employed during the day in this laboratory.

Two samples of air were also taken from Room 38 at nine o'clock in the morning. During the night preceding the room had been unoccupied, and no lamps had been in use up to the time of taking the samples. The bottles with 100 c.c. water were allowed to stand until next morning, and then analysed for nitrites.

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Two samples of air from Room 39 were taken at the same time as the preceding under the same conditions.

During the afternoon (at 3.30) two other samples of air were taken from this room in order to see whether any variation had taken place in the amounts of nitrites present. The samples were collected as in the previous cases. Eight Bunsen burners had been in use since 9 a.m., and were still burning at the time the air was taken for analysis. Three persons were employed in this laboratory during the day.

The amounts of nitrites absorbed by the water were determined in the usual manner. To see whether all the nitrites had been absorbed from the air in these bottles a little nitrite-free water was introduced after the above test. This water gave only a very faint colouration when treated with Griess's reagent, proving that nearly all the nitrite had been removed.

The temperature of the air was 20° C. at the time the analyses were made, and the barometric pressure was 758 m.m.

The results obtained are as follows, the nitrogen equivalent being calculated as nitrous anhydride :—

| Room. | Time of taking sample. | Capacity bottle. C.c. | C.c. of nitrite equivalent. | Parts $N_2O_3$ in 10,000 air. |
|---|---|---|---|---|
| 38 | 9 a.m. | 8980 | 8·5 | ·0140 |
| 38 | 9 a.m. | 8870 | 8·3 | 0·0138 |
| 36 | 3.30 p.m. | 8980 | 19·5 | 0·0319 |
| 36 | 3.30 p.m. | 8870 | 18·9 | 0·0315 |
| 39 | 9 a.m. | 8870 | 24·6 | 0·0408 |
| 39 | 9 a.m. | 8320 | 25·7 | 0·0456 |
| 39 | 3.30 p.m. | 8870 | 43·2 | 0·0690 |
| 39 | 3.30 p.m. | 8320 | 40·0 | 0·0707 |

On inspecting the above results we see that (1) in the air of rooms the amount of nitrites is, as a rule, very small, on a clear day as little as 0·014 part in 10,000 parts air having been found; (2) the burning of illuminating gas and the presence of people seem to cause an increase in the quantity of nitrites present in the air.

Reference has been made as to the possibility of persons being a factor in causing the increase in quantity of nitrites in the air. That nitrites are formed through human metabolism is evidenced by the fact that the water in which the hands are washed give, on the addition of Griess's reagent, a very strong test for nitrites.

Trial was made to ascertain whether during the breathing process of man nitrites are exhaled. To this end 100 c.c. of re-distilled water were placed in a large test-tube and exhaled air blown through this water from the lungs for five minutes. The water was then treated for nitrites in the usual manner. No pink-coloured solution was formed, thus showing that expired air on passing through pure water does not give an indication of nitrites. This circumstance does not, however, prove conclusively that nitrites are absent in air which has passed through the lungs. There is a great probability that air containing a small amount of nitrite in the presence of a comparatively great quantity of oxygen, on passing through water oxidises these nitrites to nitrates, or even decomposes them to nitrogen. That this is evidently so is seen from the fact that a stream of air drawn through pure water by means of suction also failed to give any indication of nitrites, though water left exposed, undisturbed in this same air, gave a very decided test.

It has also been mentioned that rain-water obtained during a thunder shower contained more nitrogen as nitrite and nitrate (*loc. cit.*, see above) than rain tested when there were no electrical charges in the atmosphere. It seemed, therefore, probable that the larger part of the nitrites and nitrates were washed from the air during a rain storm. This was proved to be the case, for two porcelain dishes, containing each 100 c.c. of water, absorbed nitrites equivalent to 10 and 11 "standards," respectively, just before a rain storm. Immediately after the rain ceased, one dish, exposed for one hour, gave an indication of 0·2 "standard," while another gave 0·4 "standard," showing that the air is very thoroughly washed during a heavy fall of rain.

It will be seen from the above that the results which I have obtained, though not numerous, deal yet with a subject hitherto little considered. Some of the determinations do not directly confirm what I had expected. Further experiment may lead to definite results; and although it is my intention to continue the investigation, I also hope that this fragmentary presentation may stimulate others to further work on the subject.

## THE SCIENTIFIC AND TECHNICAL DEPARTMENT OF THE IMPERIAL INSTITUTE.

A LECTURE was delivered at the Imperial Institute on Monday evening by Professor Wyndham Dunstan, F.R.S., the recently appointed Director of the Scientific and Technical Department, on some of the work of the Department. Sir Joseph Lister, Bart., D.C., President of the Royal Society, was in the chair, and there was a large audience, including representatives of science, commerce, and of India and the Colonies.

Professor Dunstan explained that the department was now provided with large and well equipped laboratories, occupying the whole of the west corridor of the second floor of the Imperial Institute. The equipment of this was finished at the commencement of October, and there was at the present time a staff of skilled chemists at work investigating a variety of natural products, derived from India and the Colonies, chiefly with a view to their commercial utilisation. The necessary funds for the appointment of an adequate staff to commence operations have been provided by the Royal Commissioners of the 1851 Exhibition, whilst the Goldsmiths' Company furnished the complete equipment for the laboratories, and also provided much of the apparatus. The department has therefore been created and endowed without pecuniary help from the Imperial Government. The Salters' Company had rendered important assistance to the undertaking by endowing a Research Fellowship of the annual value of £150, it being understood that the Salters' Research Fellow shall primarily devote himself to the investigation of the chemistry of medicinal plants, especially those derived from India and the Colonies. The principal work which the Department is now prepared to undertake was summarised as follows :—The scientific investigation of new or little known Indian and Colonial natural products with a view to their commercial utilisation throughout the Empire. The comparative examination with the same object of products of recognised value and importance, which, although known to occur or to be producible in India and the Colonies, are at present obtained commercially from other sources. Rendering advice and assistance to the Indian and Colonial Governments on all scientific and technical questions relating to the product, manufacture, and commercial utilisation of materials occurring throughout the British Empire. It was stated that the Indian Government had already made excellent preliminary arrangements for the exhibition of Indian products at the Imperial Institute, and for their scientific examination and technical valuation in or through the Department. Attached to the Department is a staff of specially selected scientific and technical Referees, whose advice is obtained on subjects connected with their special branches, whilst members of the staffs of a number of scientific and technical institutions in this country have furnished advice and assistance in conducting special enquiries or in supplying special information. Among the Institutions named were the City and Guilds Central Technical College, the Royal College of Science, the Government Laboratories at Somerset House, the Royal Arsenal, Woolwich, and at the Royal Mint, St. Thomas's Hospital, the Pharmaceutical Society, the Royal Indian

Engineering College, Cooper's Hill, and the Clothworkers' Research Laboratory in the Dyeing Department of the Yorkshire College, Leeds. It is intended greatly to extend this system of external reference and co-operation, to include institutions in India and the Colonies, so that the Department may gradually be developed into an Imperial Bureau of Scientific and Technical Advice, and be the means of federating scientific and technical workers throughout the Empire. An account was given of some of the more important enquiries which have already been set on foot at the instance of the Governments of India and the Colonies. The comparative value of the Indian Coal deposits and of the Indian iron ores, the improvement of Indian opium for medicinal purposes with a view to its extended employment in this country and abroad, the examination and valuation of Indian and Colonial fibres, of Indian tanning materials and dyestuffs, of essential oils and perfumes produced in Victoria, the chemical examination and therapeutic trial of important Indian and Colonial medicinal plants, the examination and valuation of Indian and Colonial timbers. At the close of the lecture the laboratories were open for inspection, and a number of interesting exhibits illustrating the work of the department were on view.

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## SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

### By W. W. ANDREWS.

In the years 1883 and 1884 two papers were published by Dr. Eugene Haanel, of Victoria College, Cobourg, Ontario, now of Syracuse University, in the *Proceedings of the Royal Society of Canada*, in which he described the brilliant results he was able to obtain in the production of the Bunsen iodide films on the blowpipe support, then proposed for the first time; namely, thin tablets of plaster of Paris made by casting sheets three-sixteenths of an inch thick on panes of glass and scratching them, before hardening, with ruled lines, so that when set they would readily break into oblongs measuring two and one-half by one and one-quarter inches. The pure white and highly polished surface of these tablets, and its great power of condensing heated gases and exhibiting the true colours, the cheapness, thermal and hygroscopic properties of the tablets, the ease with which they may be prepared and carried, and the excellence of the results when the sublimed iodides, bromides, oxides, and sulphides are deposited as coatings upon them, make them an ideal form of support in blowpipe work.

A small pit is made at one end of the tablet somewhat larger than a pin's head, and in this the ore to be tested is heated. The oxide coatings are produced by heating the substance *per se*, the bromides by adding to the substance a drop of fuming hydrobromic acid, and the iodides by adding a strong solution of hydriodic acid (made by dissolving five ounces of metallic iodine in seven ounces of water, by passing a steady stream of hydrogen sulphide through the solution while the iodine is slowly added). All who have experimented with this solution will be ready to admit that it yields superb results, but though easily renewable when one is near a hydrogen sulphide generator it is very unstable, takes a long time to prepare, and is troublesome to carry.

In 1890 Mr. F. A. Bowman read a paper before the Nova Scotia Natural History Society, in which was described a search for a solid reagent to replace the hydrogen iodide solution. He found that potassium hydrogen sulphide or any alkaline sulphate, which does not yield a coating of its own, mixed with potassium iodide would do very well. He also found that micro-

cosmic salt and potassium iodide gave good results. This mixture is a favourite one with some blowpipe experts. Tin is the only metal in the three series of the periodic table, beginning with copper, silver, and gold, which does not yield a characteristic coating with this reagent.

The writer has not been able to find whether there have been any other reagents besides these seriously proposed. Plaster of Paris as a support is mentioned in Moses and Parsons' late work as an alternative to charcoal. This is, as far as known to the writer, the only standard work in which the colours of the films on the tablets are described.

In the rapid development of other methods in chemical work the blowpipe has fallen largely into disuse, and for many years, besides the work outlined above and that of Col. Ross and some valuable tests for individual elements proposed by Chapman, little or no advance has been made. There are two possible lines of future progress in blowpiping, one in the direction of increased power and simplicity, so as to make the method more valuable for the field work of the mineralogist, geologist, and prospector, and the other in the direction of increased range and delicacy until the dry way tests rival the delicacy and distinctiveness of the wet tests, as they surpass them in expeditiousness. It may not be amiss, therefore, to call attention to the instrument of Plattner and Berzelius, which, in its modern form as the hot-blast blowpipe, and with the new support and the new reagents and reactions now known to chemistry, is an instrument surpassed by the electric furnace only.

The cleanliness of the method here described, as compared with the charcoal method, and the quickness with which sure results can be obtained with very small amounts, should call the blowpipe back to the table of the chemist for preliminary and confirmatory tests, to class work as an accompaniment of the wet methods, and to the lecture table for the purposes of illustration. It is possible to detect five or six metals in presence of each other on one tablet. Many of the coatings are permanent, and are all renewable on re-heating with addition of a drop of the reagent, so that a set of tablets carefully labelled with a pencil forms a permanent record of a set of experiments. The value of this to the practical chemist and to the student need not be emphasised. It may be noted that blowpiping is so much of an art that new methods are seldom well enough practised by those who have become skilful in other methods to reveal their value.

The extensions of the plaster of Paris method here proposed are—A set of new reagents, which yield some new reactions which are of value in detecting elements in the presence of each other, notably gold and copper in very small amounts in the presence of all elements so far experimented with; arsenic, tin, and antimony in presence of each other; sulphur in the presence of selenium and tellurium, and chlorine, bromine, and iodine in the presence of each other; a new set of film tests which are found to be of great delicacy (the limits of delicacy are now being measured, it being found that gold, one part in one million, and copper, one part in four millions, are easily detectable); a change in the composition of the tablets which does away with the necessity for using platinum wire in the production of the coloured glasses with borax and metaphosphoric acid, these being formed on the tablets with a decided gain in facility and delicacy; and lastly, several new methods of handling the tablets themselves.

It is evident that solid reagents will always be the more convenient to carry afield, but in the laboratory liquids are to be preferred, since they are more readily applied, and when the assay is heated the reagent, which has soaked into the tablet, is fed steadily toward the hot portion of the tablet, so that the heated assay is constantly enveloped in the vapour of the reagent. For over two years the writer has used with satisfaction the following reagents, which have been selected from a score of

experimental ones. They are stable and almost odourless, can be carried to the field in a solid form and so used if need be, while a few seconds suffice to prepare them in liquid form if it be desired so to use them.

The chief reagent is a saturated solution of iodine in a strong solution of potassium thiocyanate in water. The solution takes place almost instantly and with great absorption of heat. The bottleful now in use has been in use for over two years, a little of one or other of the ingredients being added from time to time as seemed to be required. Exact proportions are not necessary to the efficiency of the reagent. It can be prepared on the field from the solid chemicals at a moment's notice. The brilliancy of the iodide films produced with this solution are not one whit behind those possible with the pure solution of hydriodic acid. Its coatings tend to form in definite bands of colour. The spheres of deposition of the iodide and the oxy-iodide are sometimes very well defined. Some striking and important variations are produced by the presence of the potassium thiocyanate, for example, with molybdenum, osmium, iridium, tin, antimony, lead, bismuth, cadmium, and mercury.

Dr. Haanel showed in his second paper that by means of hydrobromic acid, copper and iron could be detected at one operation in the presence of each other, and in the presence of nickel and cobalt and any other flux-colouring substances. Instead of the fuming acid with its dangerous properties, a mixture in molecular proportions of powdered potassium bromide and metaphosphoric acid, or potassium hydrogen phosphate or sulphate may be used. This, suggested by Bowman's work, suggests further a set of solid reagents, made by using potassium chloride, potassium fluoride, and potassium iodide with metaphosphoric acid, and these form a valuable set for special tests. They have the advantage of yielding at once the coloured flux and the coatings produced by any volatile matter in the assay. When heated the reaction represented by the following general equation takes place—

$$KX + HPO_3 = KPO_3 + HX.$$
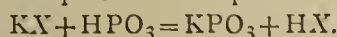
These two reagents, the iodine solution and the bromide mixture, suffice for the production of coatings. The following which are used to differentiate them, are dropped upon the oxide or iodide film and coloured spots are produced, or the colour is discharged to white (technically, *wiped*), or the coating disappears through solution and absorption by the tablet.

Dr. Haanel used ammonium hydroxide and yellow ammonium sulphide for the purpose of testing the solubility of the films and to produce the sulphide spots. Both of these are troublesome to carry, and the latter is objectionable on account of its intolerable odour, its instability, and the fact that for its renewal the hydrogen sulphide generator is required. It has been found that a solution of potassium sulphide, strong enough to show a clear amber colour, made by dissolving the solid potassium sulphide in water, or by boiling a strong solution of potassium hydroxide with an excess of flowers of sulphur till the solution assumes a blackish colour, which on cooling will be amber yellow, fulfils all the required conditions. If through the action of light it is decomposed, all that is necessary for its renewal is to boil the solution and perhaps add a little sulphur. We therefore have a reagent which can be carried as a solid, can be renewed anywhere, is as efficient as the ammonium sulphide solution, and is almost odourless.

In the place of ammonium hydroxide a solution of potassium cyanide is used, made a little more stable by the addition of a little ammonium or potassium hydroxide. Besides these the common acids of the laboratory are useful, and a solution of potassium thiocyanate.

The potassium thiocyanate solution is used in two ways. It is either dropped on the coating to test its solubility and to note the colours produced after heating, or it is dropped on the tablet before the coating is deposited, and then the hot vapours sweeping over the moist spot give with some metals characteristic reactions.

Those coatings which are pure white, and therefore invisible on the white tablet, are examined on a tablet which has been smoked in a flame, or on one streaked up the middle by means of a glass rod which has been dipped in a solution of boric and metaphosphoric acids mixed with lampblack or bone charcoal. In this way the coatings may be viewed on a white and on a black surface at the same time.

In order that the coloured fluxes may be made on the tablets, the latter must be made more resistant to the dissolving effect of the metaphosphoric acid and the alkali in the borax. If one teaspoonful of boric acid be added to each quart of the water used in making the tablets, they will be found to be denser and to have the necessary quality. Borax can be fused on them without gathering any impurities from the plaster, and if metaphosphoric acid be substituted for phosphor salt, we have a flux which will spread upon the tablet and exhibit the colours of all degrees of saturation at the same time. This reagent, first proposed by Ross, who described its reactions, is preferable to microcosmic salt, since, as it contains no volatile matter and melts readily to a clear glass, it will show by effervescence the presence of water or carbon dioxide, or other gas in a mineral. With cobalt it yields a fine violet when cold, which becomes blue on the addition of any of the alkali metals, for which, therefore, it furnishes a ready test. The only objection to this reagent is the tendency of the sticks to deliquesce, but a piece can be kept in a corked test-tube,* which can be readily dried over the flame, if dampness should gather. In dry weather it causes no trouble. Its solvent power is very great, and the colours are fine. Ross asserts that silica and zirconia are the only oxides which are not soluble in this flux. The whole operation may be completed in the time usually required to form the bead in the platinum wire loop, and the volatile oxide films will be found on the tablet above the glass, where they may be tested with potassium sulphide and the other reagents. One operation, therefore, suffices for the determination of the volatile acid elements, the volatile metal or metals, and flux-colouring metal. Metaphosphoric acid well replaces potassium hydrogen sulphate in the operation as described in most text-books for the detection of carbon monoxide, carbon dioxide, iron, chlorine, bromine, iodine, nitrogen tetroxide, chlorine tetroxide, sulphur dioxide, hydrogen sulphide, hydrocyanic acid, and acetic acid.

(To be continued).

## THE PURITY OF LONDON WATER.

AT a recent meeting of the County Council the recommendation of the Water Committee that the Council's chemist should make three examinations weekly, for a period of six months, of the water supplied by each of the London water companies was adopted, though not without considerable discussion. In view of the expenditure of the ratepayers' money thus authorised, it may be interesting to consider briefly some of the results obtained by the Council's chemist and by other chemists employed on its behalf during last year, when a series of examinations similar to those now ordered was carried out. These results are contained in a large pamphlet, elaborately provided with tables and diagrams, which was ordered to be printed in May last and has recently been issued.

The general position adopted by Mr. Dibdin, the Council's chemist, in this report is that the examinations now regularly conducted by Dr. Frankland, the official analyst, and by the two eminent chemists employed on behalf of

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* In this laboratory each student is supplied with a set of very small dipping tubes and a wooden block, into which holes are bored for the reception of a set of test-tubes closed with paraffined corks, to hold the reagents.

the companies, are incomplete, and therefore misleading. The incompleteness appears to consist in the fact that Dr. Frankland either ignores altogether, or else does not show in a manner satisfactory to the Water Committee, the amounts of suspended matter contained in the water, while the companies' chemists systematically write the word " None " in the column of their reports provided for the record of the suspended matter. The Council's chemist, on the other hand, contends that improved methods have enabled him to detect and measure a substantial amount of suspended matter in the filtered water supplied to consumers. Further, he holds it proved that the quality of the filtered water varies directly as that of the river water at the intakes near Sunbury, and considers it established that the existing arrangements for purifying the water are inadequate, particularly during periods of storm.

To take the second point first, Mr. Dibdin's conclusion is scarcely borne out by the facts and diagrams he himself supplies. According to the report the *maximum* quantity of suspended matter found at the beginning of the inquiry last year was 0·038 grains per gallon in the Southwark Company's water, there being 0·014 in the Chelsea Company's, and a little less in the Lambeth Company's, while the West Middlesex, New River, and Kent Companies' supplies contained from 0·004 to 0·002 grains per gallon. But towards the end of the inquiry, when the unfiltered water in the river was at its worst, none of the companies' supplies contained more than 0·006 grains, the average being 0·003. These statements, though they are Mr. Dibdin's own, do not altogether agree with the diagram he gives at the end of the book; they appear to prove, if they prove anything, that, so far from the filtration processes employed being inadequate during storm periods, it is precisely at storm periods that they are most efficient. This conclusion, it may be remarked, is probably not true in fact, but as it follows naturally from Mr. Dibdin's figures, it is not calculated to promote complete confidence in his methods and results.

Then as to the offending word " None " used by the companies' chemists. It must be remembered that purity in a chemical sense is entirely a relative term. It may almost be said that an absolutely pure substance is not known and has never been obtained. When a chemist pronounces a material pure he always speaks with reference to the use to which it is to be put. A substance, for example, which might fairly be designated pure if intended for use as an artificial manure, might be impure for the purposes of a chemical manufacturer, just as one reckoned pure for experiments in a school-laboratory would be quite worthless to the chemist engaged in the finest analytical work. So in the case of the suspended matter in London water. By the word " None " the chemists do not intend to imply its complete absence; they only mean to express their opinion that in view of the purposes for which the water is to be employed the amount of matter it holds in suspension is so small that it may safely be disregarded. A short scrutiny of Mr. Dibdin's figures will be enough to convince most people that the chemists are quite justified in their statement. According to him the average amount of suspended matter supplied during the year 1895 by the three companies that show the best results was 0·0011 grains a gallon. This amount he treats as an unavoidable *minimum*, and, using it as a sort of standard by which to judge other waters, deducts it from the 0·0033 grains which was the average quantity present in the water supplied by the five other companies. Thus he reaches the conclusion that these companies supplied in every gallon 0·0022 grains of avoidable suspended matter. This amount does not look very grand, so he proceeds to present the result in a way which makes it bulk more largely. Estimating that about 131 million gallons of river water are supplied to London daily, he calculates that in the course of a year nearly seven tons of chemically dry suspended matter, which

might be avoided, are distributed amongst Londoners by the water companies, or if the amount that is unavoidable be included about ten tons. But Mr. Dibdin would have the point put still more imposingly. He therefore adopts the expedient of adding 90 per cent of water to the dry matter, and is thus able to show that the people of London have supplied to them with their water the magnificent weight of 67·5 tons of avoidable " wet mud," or about 100 tons in all. If the computation of the supply of " wet mud " be made on the basis of the highest amount of matter found at any time during the year—viz., 0·0385 grains in the Southwark Company's water, Mr. Dibdin shows the result is 1145 tons, but he omits to add that were it made on the basis of the best water supplied by a company depending exclusively on the Thames the total would be about 15 tons of wet mud or 30 cwts. of dry matter.

The bacteriology of the water has also engaged the attention of the Council's chemist and those associated with him. Here, too, they have succeeded in obtaining results eminently satisfactory to themselves. They have found far more bacteria than did the official analyst and the companies' chemists, and their success inclines them to pronounce the latters' methods inadequate and their results untrustworthy. In explanation of the increased number of bacteria detected it is explained that, in the first place, the cultivations were made in such a way as to bring out all the microbes which will develop on a gelatine plate, instead of merely counting those which are self-evident in two days at ordinary temperatures, and, in the second place, that the samples were drawn from the companies' mains, not from the filter-wells and pumps. Of these two reasons probably the second is the more significant, though scarcely in the way Mr. Dibdin intends. The most elaborate bacteriological examination was carried out by Dr. Klein during eight weeks at the beginning of the year, but, unfortunately his results and those obtained in the Council's laboratory are not presented in such a form as to render comparison possible to any great extent. Dr. Klein's figures, however, in themselves are sufficiently puzzling. It is not quite obvious, for instance, why the number of bacteria present in 1 c.c. of water during one week should be 17,920 in one case, 16 in another, and 260 in a third, when all the three companies concerned draw their water from practically the same intake. Or take another question. Dr. Klein counted the microbes after three or four days' incubation in the first three weeks, but after only forty-eight hours in the last five. On the County Council theory that two days' incubation is not enough to develop anything like the full number of microbes, one would expect the average number of microbes present weekly in all the companies' waters to be greater in the first three weeks than in the last five. But such is not the case; the average was highest in the seventh and eighth weeks, lowest in the second and fourth, while in the fifth and sixth there were more present than in the first.

A possible explanation of these anomalies and also of the sudden jumps which are found in the numbers of the bacteria from week to week—one company, for instance, jumps from 116 in one week to 48,512 in the next descending to 7424 in the next again—may be hazarded Every bacteriologist knows that the utmost care is required in taking samples, if the results are to be of any value. The receptacles must be sterile, and precautions must be observed to prevent contamination while they are being filled. But it does not appear at all certain that the necessary precautions were observed by the County Council. Dr. Klein, who did not collect his own samples, mentions that the water he examined was sent to him in large ordinary stoppered bottles, which are certainly not the kind of apparatus usually employed in delicate bacteriological investigations. If it should be the case that a County Council workman was simply sent to fill a number of these bottles from convenient stand-pipes according to his own lights, and without strict

measures being taken to insure sterilisation and prevent contamination, the curious results need no longer be a matter of surprise, any more than the discovery in the samples of "fragments of matter in a state of decomposition and swarming with various bacteria," or the occurrence of cotton fibres, &c. It does not militate against this suggestion that no correspondence can be traced between the numbers of microbes as stated by Dr. Klein and the efficiency of the filtration as measured by the amount of suspended matter indicated in Mr. Dibdin's diagram. Thus, according to the latter, the efficiency of the Chelsea Company's filtration remained unaltered for the third, fourth, and fifth weeks covered by Dr. Klein, yet the number of microbes he found in that company's water was 24,148, 2124, and 21,408 per c.c. for the three weeks respectively. In the sixth week the filtration became very much worse, and only began to improve again after the eighth week. Yet Dr. Klein's figures for these bad weeks are 264, 15,264, and 420 respectively. In the fourth week the Southwark Company's filtration began to deteriorate, but the number of microbes found by Dr. Klein was much less than in the preceding week. In the fifth week the filters were still worse and the microbes more numerous. But in the sixth week, while the filters had not improved, the number of microbes was barely one-twentieth of the figure for the week before.

Nor is confidence in the Council's bacteriology increased by the disagreement between the results handed in by the various investigators it employed. Drs. Klein and Stevenson, for instance, appear to have carried on investigations on samples supplied by Mr. Dibdin during the same period, from December 27, 1894, to February 21, 1895. Yet Dr. Stevenson reports that during those eight weeks there were never more than 200 micro-organisms present in 1 c.c. of the Kent and West Middlesex waters, while Dr. Klein only in two weeks found less than 200 in the same waters; in every other week the number exceeded 500, and thrice, according to him, it rose to over 17,000.

A good many other criticisms might be passed on these documents printed by the Council, but enough has been said to show that the results and conclusions contained in them ought not to be blindly accepted without examination. Not only are they in many cases inconsistent with each other, but they are at variance with the deliberate opinions of some of the highest authorities of the day. Now that the Council has decided to spend more money in continuing these investigations it is to be hoped it will take measures to render its methods and results absolutely above suspicion.—*The Times*, November 10, 1896.

Appointments. — Dr. Thos. Ewan, Chief Assistant in the Chemical Department of the Northern Polytechnic Institute, has been appointed Research Chemist to the British Aluminium Company, in their works at Oldbury. Mr. H. Charles L. Bloxam, new Chief Assistant in the Chemical Department of the Goldsmiths' Institute, New Cross, has been appointed to succeed Dr. Ewan at the Northern Polytechnic.

Society of Arts. —The opening meeting of the 143rd Session will be held on Wednesday evening, November 18th, at 8 p.m., when an Address will be delivered by Major-General Sir Owen Tudor Burne, K.C.S.I., C.I.E., Chairman of the Council. The subject of the Address will be "India, its Arts, Manufactures, and Commerce." At the subsequent meetings before Christmas, the following papers will be read:—"Recent Developments in Mechanical Road Carriages," by W. Worby Beaumont, M. Inst. C.E.; "The Teaching of Economics," by W. A. S. Hewins, M.A.; "Mining at Great Depths," by Bennett H. Brough, Assoc.R.S.M.; "The Chamber Music of Purcell, Handel, and Bach" (with illustrations on the original instruments for which it was written), by Arnold Dolmetsch.

# CORRESPONDENCE.

## CHEMICAL EDUCATION IN ENGLAND AND GERMANY.

### *To the Editor of the Chemical News.*

SIR,—I have been much interested lately in the articles in the CHEMICAL NEWS relating to the question of why Germany stands so prominently before the world as a leader in both theoretical and practical chemistry. This question is an important one to Americans as well as Englishmen, and I, for one, should like more light on the matter. It is a fact that here in America, to the best of my knowledge, the rank and file of the chemical profession are very badly paid.

I *hope* that we are making a campaign of education here,—that is, educating the employer to realise the value of research work and pay for it. I look upon the chemist who is capable of original work as the man we should seek to produce in our schools, and who ought to be paid for his ability afterward. To me it seems that most employers make their mistake in employing a man of limited education for any except the roughest work. It is continually impressed on me that even the most unskilled work in a laboratory ought to be *closely* supervised by a man of intelligence and originality. Valuable suggestions are constantly coming to an educated man from the most unlikely sources. I do not mean to state that I think employers should engage men at high prices for routine work; but I do mean to say that a well-paid man, who has time to closely supervise *all* work done under his care, is a paying investment. In other words, we must have competently educated men,

It is a question in my mind whether our schools and colleges produce such men in as large numbers as they ought, considering the time and money spent.

Sir Henry Roscoe strikes at the root of the matter when he says that the students come into the colleges and universities very badly prepared when compared with their German brethren. I should like to suggest that a discussion of this matter of chemical education be opened in the columns of your paper. What should be studied to produce the most efficient chemist? This question, it seems to me, has been too largely left in the hands of the teachers. With all due respect to them I think, as a class, they lack many ideas that practical chemists could give them. It seems to me that all chemists should consult together to produce what I might call a framework for a universal course in their branch of Science. The advice of every thinking chemist is needed to produce the desired result. The trouble with our chemical studies at present seems to be that they are devised by men who lack experience. This is necessarily so as long as one man's ideas and experience are used. To illustrate what I mean, I will assume that a man has graduated at some good university at home, and then followed it up with study abroad. This man enters, we will say, the iron business, and spends some years in that line. He finally decides to teach, and entering some college he maps out a course in chemistry. This course will almost inevitably be warped out of shape by his experience in the iron business. The man who had spent years in the fertiliser business would naturally lean toward the studies he found most valuable to him in his former work; and so on along the line. Be the business iron, lead, greases, dyes, drugs, paints, soaps, sugars, food-stuffs, or any of the other lines open to the chemist, I think, in almost every case, the judgment is influenced and the value of the course of study impaired by coming from a man who, at best, has been able to follow but a few lines of one great subject. The average chemical student has no certain line of work that he knows he will follow after he leaves college, or if he has he never knows how soon he may be called to extend his own branch to cover other lines of work.

Surely the devising of a course of study that shall put a chemist in the position to follow out for himself any branch of chemistry is something worthy of the best work of the best chemists. No student can expect to master any branch of his subject while in school; but it seems as if, in that time, he ought to have his work so arranged that he would be competent to pursue his work along any line he might be called upon to follow. This is not the case in several institutions that I know about, and I suspect the required conditions are met by very few anywhere.

A discussion of the most essential studies for a chemist's calling may seem more fitted for a periodical devoted to pedagogics; but I feel sure the place for it is in such a paper as the CHEMICAL NEWS, that both practical and so-called theoretical chemists read. We need in this matter the best advice of each. Such a discussion could scarcely fail to be of profit to the whole profession. —I am, &c.,

A. C. BEEBE.

Savanna, Illinois, U.S.A.,
    October 26, 1890.

## THE DETERMINATION OF SULPHURIC ACID·

*To the Editor of the Chemical News.*

SIR,—In working out the process described (CHEM. NEWS, lxxiv., pp. 187—188) I find that, under certain conditions, there is a reversal of the reactions.

The affinities of the $BaSO_4$, $BaCrO_4$, and $Ag_2CrO_4$ seem so closely balanced that conditions of temperature, concentration of solution, or the mass-action of excess, a well as the sequence of the reagents, seem to determine whether one or other of the substances shall be formed or shall persist.

Further details will be submitted. Meanwhile I shall be glad to exchange observations with any reader who may have tried the process.—I am, &c.,

JAMES EDMUNDS.

29, Dover Street, Piccadilly.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 17, October 26, 1896.

The President opened the Session by announcing the death of Felix Tisserand, of the Section of Astronomy, who died on October 20th.

MM. Cornu and Sarrau were elected to join the Council for the improvement of the Polytechnic School.

Researches on Arabinose.—MM. Berthélot and G. André.—The authors conclude that under the influence of dilute acids arabinose gives rise to three orders of simultaneous reactions. 1. The formation of furfural by distillation, which differentiates the pentoses from the glucoses properly so-called. 2. The formation of humic acid, especially in closed vessels. 3. The slow formation of carbonic acid, especially marked on slow distillation.

Periodic Maxima of Spectra.—M. Aymonnet.—This paper will be inserted at some extent.

Hexamethylene-amine and some of its Derivatives.—M. Delépine.

*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Parts 4 and 5.

A New Method for the Quantitative Isolation of Alkaloids suitable for Analytical Practice.—Dr. C. Kippenberger, Private Tutor in the Technical Chemical Laboratory of the Federal Polytechnic College at Zurich. —This memoir will be inserted in full, if possible.

Application of Solutions of Iodine for the Volumetric Determination of Solutions of Alkaloids.— Dr. C. Kippenberger.

Contributions to a Knowledge of the Rancidification of Fats.—E. Spaeth.—Already inserted.

On Messinger's Method for the Determination of Aceton.—H. Ch. Geelmuyden. — This paper will be inserted if space permits.

A New Baryta Tube.—H. Ch. Geelmuyden.—This paper requires the accompanying figure.

Valuation and Standardising of Permanganate Solutions.—Prof. Dr. Riegler.—Already inserted.

Testing Bergamot Oil as to its Purity.—Prof. Dr. Arthur Bornträger.—A difference of opinion as to the possible composition of bergamot oil.

## MEETINGS FOR THE WEEK.

WEDNESDAY, 18th.—Society of Arts, 8. Opening Address of the 143rd Session, "On the Arts, Manufactures, and Commerce of India," by Major-General Sir Owen Tudor Burne, K.C.S.I., C.I.E., Chairman of the Council.

THURSDAY, 19th.—Chemical, 8. " Mercury Hyponitrites," by P. H. Ray, D.Sc. " The Nitrites of Mercury, and the Conditions under which they are Formed," by P. H. Ray, D.Sc. "The Interaction of Mercurous Nitrite and the Alkyl Iodides," by P. H. Ray, D.Sc. "Crystallography of the Monohydrated Mercurous Nitrite," by T. H. Holland, "Sulphocamphoric Acid and other Derivatives of Camphorsulphonic Acid," by H. Lapworth. D.Sc., and F. Stanley Kipping, Ph.D., D.Sc.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1930.

## ANALYSIS OF AIR BY A MUSHROOM.

By Dr. T. L. PHIPSON.

IN my notes on the " Origin of Atmospheric Oxygen,'
which have appeared in the CHEMICAL NEWS and the
*Comptes Rendus* during the years 1893 to 1895, I have
endeavoured to show, from palæontological considera-
tions and direct chemical experiments, that oxygen gas—
which at present forms about one-fifth of the volume of
the Earth's atmosphere—has appeared progressively, as
the result of the vital functions of green plants. At first,
in the earlier ages of the globe, it was derived from the
lowest order of plants (*Algæ*), which, even in our day,
give, weight for weight, more oxygen than the higher
plants.

By causing various green plants to vegetate in nitrogen
gas containing some carbonic acid, I became convinced
that they are essentially anaërobic, that they can vegetate
without free oxygen, that they were the means by which
Nature has provided the atmosphere with free oxygen
gas, and that, as the composition of the air gradually
changed, becoming more and more oxygenated with the
lapse of centuries, plants of aërobic nature and animals
appeared.

If I place over water in a glass bell full of *nitrogen
containing some carbonic acid*, a green plant such as
*Convolvulus arvensis* or *Lysimachia nummularia*,* for
instance, soon the atmosphere of the bell will be proved
to contain oxygen, and in a few months it will be even
richer in oxygen than the external atmosphere.

In *Agaricus atramentarius*, on the contrary, we have the
example of a plant (animal ?) composed of aërobic cells
which cannot vegetate without free oxygen, and which is
capable of analysing the air as completely as does a stick
of phosphorus.

Thus, if I place over water in a graduated glass bell
full of air (that is, *nitrogen containing some oxygen*) one
of these mushrooms (which is entirely plunged in the air,
*i.e.*, not in contact with the water), and expose it to the
solar light as I did with my green plants, I soon remark
a considerable condensation of water-vapour, and then
all the oxygen is absorbed; the carbonic acid produced
being dissolved in the water, the latter rises in the bell-
glass. For instance, in a small bell-glass of 200 c.c.
capacity, the level of the water, in a few days, will be
160 c.c., and remain there. The bell-glass contains then
only nitrogen, and the mushroom will dry up in it, and
can be preserved any length of time, for its vegetation
has ceased. It is, in fact, mummified in nitrogen †

If I immediately place a green plant, such as the *Lysi-
machia* already mentioned, alongside of the *Agaricus*, I
find that in a few days the latter will sometimes re-
commence slowly to vegetate; but the green plant
providing more oxygen than the mushroom can utilise,
the level of the water will soon stand at 170 c.c., or 180
c.c. for instance.

These experiments, which were carried on in the Casa Mia

Laboratory during the months of September and October,
I hope to continue next season. At present I only wish
to note that an individual of *Agaricus atramentarius* will
analyse the air in a few days as completely as will a
stick of phosphorus; because this mushroom, with its
aërobic cells, can only live in an atmosphere containing
free oxygen, and instead of pouring oxygen gas into the
air, as green plants do, it absorbs this gas, converting it
into water and carbonic acid, almost exactly as does an
animal ; only with the latter, the analysis is not complete,
the animal, as we all know, dying of asphyxia before all
the oxygen is absorbed.

The Casa Mia Laboratory, Putney,
November 11, 1896.

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## SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

By W. W. ANDREWS.

(Continued from p. 243).

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*Descriptive List of Reactions Obtainable on the Tablets.*

COPPER *per se* yields with difficulty a coating of volatilised
metal. With the iodine solution it yields a white iodide
coating and an emerald green flame. The iodide treated
with a drop of potassium sulphide gives with gentle heat
a blackish grey, which is removed by greater heat.
Potassium cyanide and nitric acid dissolve the sulphide ;
hydrochloric and sulphuric acids have no effect till heated,
and then they remove the spot. Potassium thiocyanate
applied to the coating has no effect till heated, when a
grey spot is shown. Any part of the coating touched
with the tip of the flame shows the emerald green flame
(Haanel). Metaphosphoric acid glass is greenish-blue
when hot and a fine robin's egg blue when cold. Meta-
phosphoric acid and potassium bromide yield a splendid
reddish violet coating of copper bromide (compare
osmium). The bromide plus potassium sulphide shows a
brown, which if heated turns blackish and then green, not
affected by sulphuric acid, but immediately destroyed by
a drop of nitric acid.

Copper plus metaphosphoric acid and potassium chloride
yields a yellow brown cupric chloride, which, if treated
with a drop of potassium thiocyanate, gives a black ring,
which, if heated, becomes a black spot. If, before the
assay is heated, a drop of nitric acid be placed one-half
inch from the assay, and a drop of potassium thiocyanate
be placed above that, on heating a fine and very volatile
blue-black coating is deposited far up the tablet. This
blue-black is not affected by acetic acid, is wiped off by
sulphuric acid slowly, and immediately by hydrochloric
and nitric acid. The formula of this compound will be
determined if some method be found by which it may be
collected in quantity. (See chlorine.)

Silver gives *per se* a pinkish-grey coating, which,
touched by the blowpipe flame (flamed), becomes mottled
brown. Reduced globules are often shown. Metaphos-
phoric acid yields the same coating and a pearl-like glass.
The iodine solution yields a pale yellow, paler when cold,
and around the assay forms a black, which does not fuse
into the tablet (compare lead). Flaming with oxidising
flame yields a mottled brown anywhere on the tablet.
This is a very delicate test, and as all other coatings are
volatile, the flame drives them off and leaves the silver
oxide. Potassium sulphide produces a spotted blackish
brown, probably potassium silver sulphide, the analogue
of ammonium silver oxide, for if treated with a drop of
potassium cyanide it immediately disappears, but if it be
first heated, the potassium cyanide has no effect. If only
one-half of the sulphide spot be touched with the tip of
the flame, and then the potassium cyanide be applied, the

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* Both these plants are very good for such experiments and save
much time, especially the *Lysimachia*, which belongs to the family
of the *Primulaceæ*, several genera of which are water-plants, and the
*L. nummularia* itself — now cultivated in many gardens — requires
a good deal of water to flourish luxuriantly. The English name of
the plant is *Money-wort*.
† In Nature this *Agaricus*, as everyone knows, soon ends by re-
solving itself into a dark-coloured liquid, which has often been used
as ink for writing. An old botanist once told me it formed an
indelible ink ; but I find that chlorine turns it pale brown and finally
bleaches it. The colour is contained in the spores.

'untouched portion will disappear while the other half will remain. Potassium thiocyanate on the iodide wipes it off; when heated the spot turns black, which is not wiped off by potassium cyanide.

Gold is slightly volatile *per se*, and more so if a solution of iodine in potassium iodide be used as a reagent, and the result is a fine rose-coloured film of the metal. If potassium thiocyanate be present no volatility is noticed. Gold and the other elements which respond to the new tests will be the subject of another paper.

Zinc *per se* yields a white coating, not very volatile, and luminous yellow when hot. Potassium sulphide and potassium thiocyanate produce no visible change on zinc films. The iodide film is a white, which treated in any part with cobalt nitrate solution yields the well-known zincate of cobalt, which is quickly decomposed by a drop of nitric acid (compare tin). This reaction obtained in this way is decisive for zinc, as aluminum and silicon do not volatilise, and are therefore not present in the coating. In the metaphosphoric acid glass, zinc causes flashes of light and detonations (Chapman). Metallic zinc sometimes yields *per se* a black sublimate along with the white oxide (compare arsenic).

Cadmium *per se* yields one of the most beautiful of the oxide films, which consists of a rich brown with black farther away and somewhat iridescent near the assay. Acetic acid does not affect it; potassium cyanide dissolves it at once (compare cadmium sulphide). Potassium sulphide and potassium thiocyanate yield a scarlet when hot, and bright yellow cold. This cadmium sulphide is not affected by potassium cyanide, is quickly destroyed by nitric acid, less readily by hydrochloric acid, immediately by acetic acid (compare cadmium oxide), and is not affected by sulphuric acid (compare copper).

The iodide coating is white with well-defined borders, which is easily distinguished in the presence of other white coatings by the *per se* and sulphide reactions. In the assay and near it the sulphide reaction will be seen caused by the potassium thiocyanate in the iodine solution (see sulphur). In metaphosphoric acid cadmium acts like zinc, and yields at the same time its oxide coating beyond the glass.

Mercury gives *per se* a very volatile film of mercury snow, which, with a feather, may be swept into a globule. It is not affected by the other reagents.

The iodide coating is a splendid combination of scarlet, yellow, and velvety green. This is caused by the mixing of the green mercurous iodide with the scarlet and yellow forms of the mercuric iodide. The reactions of each kind of iodide may be obtained on the one tablet. The green and the scarlet are the stable forms into which the coating changes on standing. A drop of the reagent or some more of the vapour blown across the coating changes all into the scarlet form. With mercurous iodide, sulphuric acid gives a yellow spot (mercurous sulphate). Potassium hydroxide gives a black; so does ammonium hydroxide (iodomercuramine, $NH_2Hg_2I$), and potassium sulphide. With the mercuric iodide, sulphuric acid increases the amount of the scarlet, potassium hydroxide yields a white, as does ammonium hydroxide (iodomercuramine) and potassium sulphide, yield a white spot quickly turning black. The sulphide spot, strange to say, is partially dissolved in nitric and hydrochloric acid, while sulphuric acid turns it brownish. Potassium cyanide yields a black, and potassium thiocyanate a dark spot, and if heated both are wholly volatilised (compare lead, bismuth, and silver). Water has no effect on this coating (compare lead), nor have hydrochloric, nitric, or sulphuric acids. By the last the coating is not readily wetted.

Gallium has not been experimented with. Indium yields a pale yellow iodide coating and a blue flame.

Thallium *per se* yields a feathery brown with white farther away and a green flame (compare arsenic and tellurium). Potassium sulphide gives a terra-cotta brown spot with a black ring. Potassium cyanide and potassium thiocyanate have no effect upon it. The iodide film is an

egg yellow with a purple black veil farther away. Potassium sulphide gives a rich brown which potassium cyanide darkens. Hydrochloric acid discharges it slowly and yellow is left (compare bismuth and tellurium). Potassium thiocyanate has no effect on the yellow or the black till heated, when it yields a white (compare bismuth, tellurium, tin, and lead). Potassium cyanide dissolves the black, but has no effect on the yellow. Sulphuric acid has no effect. A drop of the reagent on the coating heated shows a spreading black and an orange ring.

Carbon yields a sooty coating, which comes better if sulphuric acid or metaphosphoric acid be used upon the assay. In the case of the carbonates, boric oxide or metaphosphoric acid yield an odourless effervescence (Ross, Chapman). Organic acids blacken the tablet when heated.

Silicon.—An interesting reaction given by the silicates, especially the hydrous forms, is being investigated. Chapman dissolves a silicate in boric oxide and then precipitates the silica by adding metaphosphoric acid.

Germanium will give a light yellow iodide film, but none has been on hand to experiment with.

(To be continued).

# SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.*

## By GEORGE AUCHY.

(Continued from p. 215).

*Volhard's Method.*

THE fact brought out by working upon Stone's method, that titration in faintly acid (nitric) solution gives too high results led to the suspicion that the same was also true of Volhard's regular method (sulphuric acid solution). The following tests were made :—

TABLE V.

| No. | Volhard. Zinc oxide added to coagulation. | Volhard. Zinc oxide in large excess. |
|---|---|---|
| 490 | 0·49 | 0·39 |
| 490 | 0·49 | 0·39 |
| 490 | 0·49 | 0·39 |
| 490 | 0·49 | 0·49 |
| 476 | 0·51 | 0·46 |
| 507 | 0·49 | 0·44 |
| 483 | 0·45 | 0·41 |
| 503 | 0·45 | 0·41 |
| 471 | 0·41 | 0·38 |
| 289 | 0·42 | 0·40 |
| 289 | 0·42 | 0·40 |
| 493 | 0·51 | 0·44 |
| 505 | 0·50 | 0·46 |
| 155 | 0·58 | 0·49 |
| 155 | 0·58 | 0·56 |
| 289 | 0·42 | 0·41 |
| 153 | 0·66 | 0·64 |

Results of the first column were obtained by adding zinc oxide till the solution stiffened and the iron all precipitated. In the second column of determinations the zinc oxide was added in sufficient excess of this amount to make the colour of the precipitated iron a light brown. The differences in the results were supposed to be due to this fact, already noted in considering Stone's method, —that titration in slightly acid solutions gives too high results. But a suspicion arose that these differences might, in part at least, be due to manganese being mechanically carried down with the iron when the large excess of zinc oxide was used. The obvious test of this

would have been to make gravimetric determinations in the samples used in the last table. But, unfortunately, there remained but very little drillings of each of the samples. So the next best thing was done, and a standard manganese sample was prepared, and the determinations of these samples of the last table made by the colour method; in each case making a number of tests and taking the average. Results:—

### TABLE VI.

| No. | Volhard. Zinc oxide to coagulation. | Volhard. Zinc oxide in large excess. | Colour method. |
|---|---|---|---|
| 490 | 0·49 | 0·39 | 0·48 |
| 507 | 0·49 | 0·44 | 0·435 |
| 483 | 0·45 | 0·41 | 0·43 |
| 503 | 0·45 | 0·41 | 0·423 |
| 471 | 0·41 | 0·38 | 0·38 |
| 289 | 0·42 | 0·40 | 0·40 |
| 492 | 0·51 | 0·44 | 0·46 |
| 503 | 0·50 | 0·46 | 0·49 |
| 155 | 0·58 | 0·49 | 0·56 |

Showing that when the neutralisation with zinc oxide is carried only to the point of precipitating the iron the result will invariably be from 0·01 per cent to 0·05 per cent too high; while, on the other hand, if the zinc oxide be added in excess of this amount, the result *may* be too low, and very much too low, from the precipitation of the manganese with the iron. These points would have been more certainly and satisfactorily proved, however, had the comparison of the Volhard results been made directly with results by the gravimetric process instead of by the colour test. In the following table such comparisons with the gravimetric method—in a new lot of steels—are made, and confirm the conclusions drawn from the preceding table. In the second column of tests, the neutralisation was performed in a way not to precipitate the manganese. In the third column of tests neutralisation was purposely performed in a way most favourable to the precipitation of manganese with the iron.

### TABLE VII.

| No. | Zinc oxide to coagulation. Per cent. | Excess of zinc oxide. The excess added after filtration of ferric oxide. Per cent. | Excess of zinc oxide. Added suddenly to the iron solution. Per cent. | Gravimetric method. Per cent. | Colour method. Per cent. |
|---|---|---|---|---|---|
| 451 | 0·56 | 0·51 | 0·51 | 0·52 (acetate) | 0·53 |
| 452 | 0·46 | 0·44 | 0·44 | 0·43 ,, | 0·435 |
| 453 | 0·46 | 0·46 | 0·37 | — | 0·425 |
| 454 | 0·47 | 0·47 | 0·44 | 0·46 (Ford) | 0·45 |
| 493 | 0·51 | 0·46 | 0·44 | — | 0·46 |
| 456 | 0·45 | 0·41 | — | 0·41 (Ford) | 0·43 |
| 466 | 0·54 | 0·49 | — | 0·485 ,, | 0·49 |
| 481 | 0·48 | 0·45 | — | 0·455 ,, | 0·46 |
| 153 | 0·66 | 0·64 | — | — | 0·64 |
| 000 | 1·30 | — | — | 1·25* | — |

* Made by Williams, of Boston.

Insufficient neutralisation gives high results. Complete neutralisation *suddenly* gives low results. Here, then, is the explanation for the low result of Table III. (483); the ferric oxide precipitate had carried down some of the manganese.

The remedy is obvious. It is to carefully avoid an excess of zinc oxide at the time of precipitating the iron; adding the necessary excess to the aliquot part of the filtrate from the ferric oxide, taken for titration—filtering off the undissolved zinc oxide before titrating. But this procedure involves considerable extra work. And it does not seem necessary, if certain precautions be taken, to filter off the ferric oxide before adding the excess of zinc oxide. For it is reasonable to suppose that it is the *sudden* addition of the zinc oxide in excess to the rather concentrated solution that carries down the manganese.

If the iron be first precipitated carefully by the gradual addition of zinc oxide, avoiding an excess, we have seen that no manganese is carried down. If now, the solution be diluted, mixed, and the ferric oxide be allowed time to begin to settle, there seems no reason why the further addition of an excess of zinc oxide should then precipitate manganese. That it does not is evidenced by the preceding table, second column of results, last four results, which were obtained in this way. Also all of the determinations by Stone's modification in Table XI.

In the determination of the results of the third column of results in the preceding table, pains were taken to add the excess of zinc oxide as suddenly as possible; nevertheless, only three out of the five results are low, showing (as also do the results of Table VI.) that manganese is not invariably carried down by such a procedure. In Stone's modification the tendency to a precipitation of manganese with the iron seems less; for of the numerous results by that method (obtained before the necessity of any precaution in precipitating the ferric oxide was known) only one is low. But in both methods the neglect of the precaution to *thoroughly* neutralise with zinc oxide almost invariably gives results more or less above the truth.

(To be continued).

## ON THE INVERSION OF SUGAR BY SALTS.*
### No. II.

By J. H. LONG.

(Concluded from p. 238).

*Ferrous Bromide.*

SOLUTIONS of this salt were made by adding the proper amount of bromine to an excess of iron and water. A reaction soon begins, which is hastened by heat. Finally the solution is thoroughly boiled, which eliminates all free bromine and leaves the iron in the ferrous condition. It is then filtered into the cold sugar solution and is ready for use. A solution so made is practically neutral.

*Experiment 22.*

$FeBr_2$. 0·54 N.
In 250 c.c., 50 grms. of sugar + 14·58 grms. of bromide.
A = 31·43.

| $t$. | $a$. | $x$. | $\log. \frac{A}{A-x}$. | $\frac{1}{t}\log. \frac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 23·13° | — | — | — |
| 15 | 16·76 | 6·37° | 0·09836 | 0·00655 |
| 45 | 9·76 | 13·37 | 0·24062 | 0·00534 |
| 75 | 6·07 | 17·06 | 0·33988 | 0·00453 |
| 105 | 4·00 | 19·13 | 0·40743 | 0·00388 |
| 165 | 0·68 | 22·45 | 0·54406 | 0·00329 |
| 285 | −4·03 | 27·16 | 0·86691 | 0·00304 |
| 345 | −5·60 | 28·73 | 1·06598 | 0·00309 |

*Experiment 23.*

$FeBr_2$. 1·04 N.
In 250 c.c., 50 grms. of sugar + 28·08 grms. of bromide.
A = 29·50.

| 0 | 21·20° | — | — | — |
|---|---|---|---|---|
| 15 | 13·60 | 7·60° | 0·12938 | 0·00862 |
| 45 | 6·22 | 14·98 | 0·30785 | 0·00684 |
| 75 | 2·90 | 18·30 | 0·42060 | 0·00561 |
| 105 | 0·75 | 20·45 | 0·51317 | 0·00489 |
| 165 | −2·70 | 23·90 | 0·72163 | 0·00437 |
| 285 | −6·35 | 27·55 | 1·17979 | 0·00414 |
| 345 | −7·50 | 28·70 | 1·56673 | 0·00454 |

The normal solutions here invert but little faster than the half normal. The rates in both cases diminish

rapidly from the start, but after the middle of the inversion become nearly constant, as was observed with the ferrous chloride. The first three of the solutions taken from the thermostat had to be filtered before polarising.

### Ferrous Iodide.

A half normal solution was made by mixing 15·87 grms. of iodine with an excess of iron and water, in the usual manner. On complete disappearance of the iodine the solution was boiled and filtered into a cold sugar solution. Water was finally added to make the volume up to 250 c.c. The amount of sugar present is not sufficient to prevent some decomposition on heating, but, as in the other cases referred to, the turbidity at first noticed disappeared after longer warming in the thermostat. The first polarisations were made after filtering, and those later were made directly.

### Experiment 24.

$FeI_2$.  N/2.

In 250 c.c., 50 grms. of sugar + 19·37 grms. of iodide. A = 32·03.

| $t$. | $a$. | $x$. | $\text{Log.} \dfrac{A}{A-x}$. | $\dfrac{1}{t}\text{log.}\dfrac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 23·73° | — | — | — |
| 15 | 17·45 | 6·28° | 0·09478 | 0·00632 |
| 30 | 13·57 | 10·16 | 0·16571 | 0·00552 |
| 45 | 11·62 | 12·11 | 0·20627 | 0·00458 |
| 60 | 9·73 | 14·00 | 0·24956 | 0·00416 |
| 90 | 7·50 | 16·23 | 0·30690 | 0·00341 |
| 150 | 4·40 | 19·33 | 0·40176 | 0·00268 |
| 270 | 0·90 | 22·83 | 0·54177 | 0·00200 |
| 390 | −2·80 | 26·53 | 0·76520 | 0·00196 |

In my former paper a preliminary experiment with ferrous iodide was described in which the coefficient appeared to be nearly constant and much smaller than here. The experiments are, however, not comparable, as in the former case the sugar solution was very strong, containing, in 250 c.c., 125 grms. of sugar. In such a solution the degree of dissociation of the iodide would be necessarily very different from that in a weaker solution. In the strong solution no separation of ferrous hydroxide or other compound appears, even on warming. A strong syrup is much more stable than a weak one, and the lower rate of inversion may be thus easily accounted for.

### Cadmium Chloride.

One solution of cadmium chloride was tested as to its inverting power. It was made with a salt purified by several crystallisations at a low temperature, free from uncombined acid.

### Experiment 25.

$CdCl_2$.  0·94 N.

In 250 c.c., 50 grms. of sugar + 42·958 grms. of chloride. A = 29·71.

| | | | | |
|---|---|---|---|---|
| 0 | 21·41° | — | — | — |
| 15 | 12·80 | 8·61° | 0·14862 | 0·00990 |
| 30 | 6·59 | 14·82 | 0·30001 | 0·01000 |
| 60 | −1·33 | 22·74 | 0·62967 | 0·01049 |
| 90 | −4·89 | 26·30 | 0·94015 | 0·01044 |
| 150 | −7·70 | 29·11 | 1·69475 | 0·01129 |

The rate of inversion is about as rapid as with 0·002 N hydrochloric acid at the same temperature and same sugar concentration.

### Lead Nitrate.

A single test was made with a solution containing lead nitrate. The salt was re-crystallised from a pure Schuchardt specimen and was weighed in proper amount directly.

The coefficient here is found to increase very rapidly, as was noticed by Walker and Aston in their experiments (*loc. cit.*), which were carried out with a half normal nitrate solution at 80°, but with a weaker sugar solution. The mean value they give from the results of polarisation

### Experiment 26.

$Pb(NO_3)_2$.  N/2.

In 250 c.c., 50 grms. of sugar + 20·65 grms. of nitrate. A = 33·70.

| $t$. | $a$. | $x$. | $\text{Log.} \dfrac{A}{A-x}$. | $\dfrac{1}{t}\text{log.}\dfrac{A}{A-x}$. |
|---|---|---|---|---|
| 0 | 25·40° | — | — | — |
| 15 | 22·86 | 2·54° | 0·03403 | 0·00227 |
| 45 | 17·38 | 8·02 | 0·11803 | 0·00262 |
| 75 | 12·10 | ·13·30 | 0·21800 | 0·00284 |
| 135 | 2·28 | 23·12 | 0·50314 | 0·00372 |
| 195 | −3·63 | 29·03 | 0·85831 | 0·00440 |
| 345 | −7·70 | 33·10 | 1·74948 | 0·00507 |

at three intervals is 0·00159, but the inversion was not carried nearly to completeness, as in the above case.

The experiments given show in a marked manner the extreme variations in the value and constancy of the inversion coefficient, and the data obtained may be roughly tabulated as follows :—

| Potassium alum .. .. .. .. | K constant. | | |
|---|---|---|---|
| Ferrous sulphate . .. .. .. | ,, increases slowly. | | |
| Ammonium ferrous sulphate .. | ,, | ,, | ,, |
| Zinc sulphate .. .. .. .. | ,, | ,, | ,, |
| Cadmium chloride .. .. .. | ,, | ,, | ,, |
| Manganous sulphate .. .. .. | ,, | ,, rapidly. | |
| Manganous chloride .. .. .. | ,, | ,, | ,, |
| Lead nitrate .. .. .. | ,, | ,, | ,, |
| Ferrous chloride .. .. .. | ,, decreases | ,, | |
| Ferrous bromide .. .. .. | ,, | ,, | ,, |
| Ferrous iodide .. .. .. .. | ,, | ,, | ,, |

In the cases of the last three salts the values of K decrease very rapidly at the beginning of the heating, but become nearly constant later, finally, in fact appearing to increase a little. This behaviour seems to bear some relation to the stability of the salts in aqueous or weak saccharine solution. As was mentioned these ferrous halogen solutions became turbid in the thermostat, and the first three or four portions withdrawn in each case for polarisation had to be filtered. Later, the liquids became perfectly clear under the influence of longer heating.

During the turbid stage of the reaction, owing to the temporary separation of a trace of base in insoluble form, the amount of free acid present would be relatively increased, and would therefore greatly accelerate the speed of inversion. With the clearing of the solutions on longer heating the normal hydrolysis only would obtain and then the reaction should approach in regularity that due to the presence of a small constant amount of mineral acid.

It was mentioned that the solutions with ferrous sulphate and ferrous ammonium sulphate became likewise turbid on heating. But here the very slight opalescence persisted through the whole time of heating, and was perhaps greater at the end of the reaction than at the beginning. Other experiments also show in this respect a marked difference between ferrous sulphate and chloride. In my former paper I referred to solutions of these salts which had been used qualitatively. Portions of these solutions that had not been heated are still in existence. After standing eight months in the light I find that the chloride is practically clear, while the sulphate has become much changed. The bottle contains a decided flocculent precipitate. My former experiments with a strong solution seemed to indicate that at a temperature of 100° the first slight precipitate which forms disappears, but this is not true of the weaker solutions at 85°.

The slight precipitate of ferrous chloride and other halogen compounds being temporary, while that of ferrous sulphate is apparently permanent, we should expect just such irregularities in the speed of inversion as the experiments actually show. A solution of manganous sulphate with sugar becomes also slightly decomposed on heating, and the decomposition increases with the time

and temperature. At a temperature of 100° a solution of 50 grms. of sugar and 10 grms. of the sulphate in 100 c.c. become so dark that an exact polarisation is not possible, even after filtering. The solution in the present case is much less concentrated, but the precipitate is still marked and its formation is undoubtedly attended by the separation of a little free acid. We should therefore expect an acceleration in the rate of inversion as before.

These considerations do not aid us in explaining, however, the increase in K for manganous chloride, cadmium chloride, or lead nitrate. The solutions with these salts are clear and remain so throughout the reaction. In the case of manganous chloride it must be remembered that an almost complete loss of colour follows after heating. The pink fades, and in a few hours at the temperature of the thermostat becomes imperceptible in a small volume of the liquid. The colour is not restored by cooling. We have here evidently a reaction in which a change takes place in the form of combination of the manganese, with a necessary alteration in the degree of dissociation of the salt.

It is true, as already said, that most of the bases under consideration form compounds with the sugars, so that we should expect from this cause a slight disturbance at least in the apparent rate of inversion. Too little is known of the optical properties of these saccharose, dextrose, and levulose metallic compounds to say just what effect they would have on the rotation, but that they have some action is suggested by the results of some of the polarisations to determine the end-point in the inversion. This was usually found a little below the theoretical, $-8.6°$ for a 200 m.m. tube, but in several cases it was found above after prolonged heating. This was also true of a solution of sugar with manganous chloride, which stood exposed to the light several months.

It must be remembered also that solutions of dextrose are easily oxidised, and those of levulose much more so. The dark colour often seen near the end of the reaction points to such a decomposition.

It will be recognised that a determination of the hydrolysis of many of the heavy metallic salts cannot be measured with great accuracy, because of these several disturbing influences, but a comparison of some little value in the above cases may be made by considering the results obtained at the beginning of the reactions in which the coefficient is an increasing one, and near the end of the reaction in cases where it decreased and then became nearly constant. By taking the mean of the first two values in the one case, and of the last two in the other, we obtain the second column of the table below as the most probable values of the coefficient for half normal solutions.

In the third column is given a calculation of the extent of hydrolysis of the salts, expressed in per cents of total salt present, and based on a comparison with hydrochloric acid acting in 0.001 normal solution at the same temperature and on same amount of sugar. This comparison is at best a rough one, assuming as it does complete hydrolysis of the acid, and neglecting the effect of the excess of undecomposed salts on the rate of inversion.

| | K. | Salt hydrolysed in per cent. |
|---|---|---|
| Lead nitrate .. .. .. .. | 0.00244 | 0.096 |
| Manganous chloride.. .. .. | 0.00095 | 0.035 |
| Manganous sulphate . .. .. | 0.00052 | 0.020 |
| Ferrous sulphate .. .. .. | 0.00085 | 0.033 |
| Ferrous ammonium sulphate.. | 0.00068 | 0.026 |
| Zinc sulphate .. .. .. .. | 0.00040 | 0.016 |
| Ferrous chloride .. .. .. | 0.00164 | 0.063 |
| Ferrous bromide (0.54 N) . .. | 0.00300 | 0.109 |
| Ferrous iodide .. .. .. .. | 0.00198 | 0.078 |
| Potassium aluminum sulphate, N/4 .. .. .. .. .. .. | 0.01835 | 1.440 |
| Cadmium chloride (0.94 N) .. | 0.01000 | 2.080 |

The amount of hydrolysis is small in all cases except those of the alum and cadmium chloride.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

THE following are the abstracts of papers received during the vacation, and published in the *Transactions* :—

107. "*Contributions to the Chemistry of Phenol Derivatives.*" By R. MELDOLA, F.R.S., G. H. WOOLCOTT, and E. WRAY.

In this paper the authors describe a number of new derivatives of phenol, pyrocatechol, guaiacol, &c., which have been prepared incidentally in the course of an investigation into the methods of synthesis of certain natural phenol derivatives, such as eugenol, safrole, &c.

4-*Chloro-3-nitrophenol* from the corresponding nitro-aminophenol by Sandmeyer's process. Whitish needles, m. p. 126—127°. Benzoyl derivative, m. p. 96—97°. Acetyl derivative, m.p. 83—85°.

*Diacetyl-o-aminophenol* (o-acetaminophenyl acetate) prepared by heating o-aminophenol with excess of acetic anhydride and dry sodium acetate. White prismatic needles, m. p. 123—124°, or with $1\frac{1}{2}H_2O$, m. p. 76—77°. The nitro-derivative, obtained by nitrating the diacetyl compound by a mixture of ordinary and fuming nitric acid, gives, on hydrolysis, 5-nitro-2-aminophenol (Friedländer and Zeitlin, *Ber.*, 1894, xxvii., 196).

2-*Chloro-5-nitrophenol*, obtained from the last nitro-aminophenol by Sandmeyer's process. White needles, m. p. 118—119°. Benzoyl derivative, m. p. 127—128°.

2-*Bromo-4-nitro-6-aminophenol*, obtained by reducing the bromodinitrophenol, m. p. 118—119°, of Laurent and Körner by means of ammonium sulphide. Whitish needles, soluble in hot water; becomes brown on exposure to air; m. p. 162—163°. Both acid and basic in properties. Acetyl derivative, m. p. 194° with decomposition, can be made to decompose at 204° by rapidly heating. Anhydro-base; by heating acetyl derivative with acetic anhydride, m. p. 146—147°. Methyl ether (bromonitro-o-anisidine), yellow needles, m. p. 120—121°. Diazoxide; yellow needles, decomposing point 152—153°.

2-*Chloro-4-nitrophenol*, obtained from 4-nitro-2-aminophenol (Laurent and Gerhardt, *Annalen*, 1850, lxxv., 68) by Sandmeyer's process. Benzoyl derivative, m. p. 135°. Acetyl derivative, m. p. 63°.

4-*Nitro-2-aminoanisole*, prepared by reducing 2 : 4-dinitroanisole in alcoholic solution with ammonium sulphide. Orange needles (from water), m. p.) 118°. Acetyl derivative, m. p. 174—175°.

5-*Nitro-2-aminoanisole*, prepared by hydrolysing the acetyl derivative obtained by nitrating o-nitroacetaniside, (Mühlhauser, *Annalen*, 1881, ccvii., 242). Yellow needles (from water), m. p. 139—140°. Acetyl derivative, m. p. 145—146°.

*Nitroaminoguaiacol*, obtained by reducing dinitro-guaiacol, m. p. 121° (Herzig, *Monatsh.*, 1882, iii., 825) with ammonium sulphide; brown needles, both acid and basic; decomposing point 182°. Acetyl derivative, decomposing point 224—226. Diacetyl derivative, decomposing point 204°. Diazoxide; orange needles, exploding sharply at 169—170°. Constitution probably 4-nitro-6-amino-2-methoxyphenol.

5-*Nitro-3-aminopyrocatechol*, obtained by reducing the dinitropyrocatechol of m. p. 164° (Nietzki and Moll, *Ber.*, 1894, xxvi., 2183) with ammonium sulphide; acid and basic ochreous needles, m. p. 220—221° with decomposition. Diazoxide; flat, golden needles, exploding sharply at 159—160°. Soluble in alkali, with a purple

colour. The authors point out that generally the formation of diazoxides may be taken as evidence that the amino- and hydroxy-groups are ortho with respect to each other, and they consider the formula of the compound to be 5-nitro-3-amino-2-hydroxyphenol.

108. "*Action of Light on Amyl Alcohol.*" By A. RICHARDSON, Ph.D., and EMILY C. FORTEY, B.Sc.

The authors have investigated the action of light on a number of alcohols in presence of oxygen. The alcohols used were obtained from Kahlbaum, and carefully purified by re-distillation. It was found that whereas in the case of methyl, ethyl, propyl, and butyl alcohols an exposure extending over many months failed to produce any apparent change, the alcohols remaining neutral to litmus and containing no hydrogen peroxide, amyl alcohol gave strongly acid reactions and contained large quantities of hydrogen peroxide after only a few days' exposure. A similar change seemed to take place in the case of octyl alcohol, but to a very much smaller extent. The action of light on amyl alcohol was therefore studied in detail.

Amyl alcohol was exposed to light in presence of excess of water and of oxygen for a few days. A portion of the water was then tested with titanic acid, when the presence of hydrogen peroxide was shown by a deep brown colouration. Another portion was shaken with pure ether and potassium bichromate, when the ether assumed an intensely blue colour, leaving no doubt as to the presence of hydrogen peroxide in the solution. In another experiment liquid water was absent, amyl alcohol being exposed in presence of moist oxygen. Two days' exposure sufficed to bring about the formation of hydrogen peroxide, as shown by the titanic acid test. A third experiment was made with dry alcohol. A sample of amyl alcohol dried first from quicklime, then by distillation from sodium, was sealed in a bent tube containing oxygen and phosphorus pentoxide (care being taken not to allow the liquid to wet the pentoxide), and kept in the dark for seven weeks. After exposure, the alcohol was found to contain abundance of hydrogen peroxide.

The other products formed were then examined. The acidity was found to be due to the presence of valerianic acid, and the absence of carbon dioxide leads to the conclusion that the change is one of a comparatively simple nature, not involving the breaking down of the molecule. It seems, then, that the products formed by the oxidation of amyl alcohol in presence of sunlight and oxygen only differ from those formed when other oxidising agents are used in that hydrogen peroxide is formed instead of water. The change may, therefore, be represented by the following equation :—

$$2C_5H_{11}OH + 3O_2 = 2C_4H_9COOH + 2H_2O_2.$$
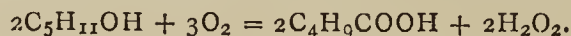
It was found that the presence of sunlight was essential to the change, a sample of amyl alcohol kept in the dark at 100° for nine days remaining neutral to litmus, and containing no hydrogen peroxide.

109. "*Note on the Action of Light on Ether.*" By A. RICHARDSON, Ph.D., and EMILY C. FORTEY, B.Sc.

Ether prepared from pure alcohol and pure sulphuric acid, and then treated with potassium bichromate, was dried by repeated distillation from phosphorus pentoxide in a specially constructed apparatus by means of which samples could be sealed for use without contact with air. The ether was then exposed in a tube containing oxygen which had been dried by contact with phosphorus pentoxide for many weeks. After three days' exposure the liquid gave a well-marked peroxide reaction when tested with titanic acid.

In order to investigate the other products formed, a sample of ether was exposed for many weeks in presence of water and oxygen. It was then rich in hydrogen peroxide, and gave an acid reaction with litmus. The neutralised solution was distilled on the water-bath. The distillate, consisting chiefly of ether, was also proved to contain aldehyde by its reducing action on ammoniacal

silver nitrate, and by its restoring the colour to rosaniline hydrochloride, decolourised by sulphurous acid. The residue in the distilling flask gave a distinct red colour with ferric chloride, and the characteristic smell of ethyl acetate on warming with alcohol and sulphuric acid, leaving no doubt as to the formation acetic acid. No carbon dioxide was formed in the reaction, which may, therefore, probably be represented by the equation—

$$2(C_2H_5)_2O + 5O_2 = 4C_2H_4O_2 + 2H_2O_2,$$
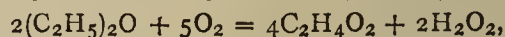
aldehyde being an intermediate product.

Here, again, hydrogen peroxide takes the place of the water which is formed when ordinary oxidising agents are used.

110. "*The Constitution of Lapachol and its Derivatives.* Part III. *The Structure of the Amylene Chain.*" By SAMUEL C. HOOKER.

Experimental proof is brought to show that the amylene chain must be written $-CH_2 \cdot CH : C(CH_3)_2$, and not $-CH : CH \cdot CH(CH_3)_2$, as has been previously assumed. In accordance with this change, new formulæ are proposed for various lapachol derivatives.

111. "*Lomatiol.*" By SAMUEL C. HOOKER.

The colouring-matter obtained by Rennie (*Proc.,* xi., 150) is a hydroxyisolapachol.

112. "*Contributions to the Knowledge of the β-Ketonic Acids.* Part II." By SIEGFRIED RUHEMANN, Ph.D., M.A., and C. G. L. WOLF, B.A., M.D.

The authors describe the products of the action of ethylic chlorofumarate on ethylic benzoylacetate, and on the sodium derivative of ethylic methylacetoacetate; of the hydrolysis of ethylic methylfurfurandicarboxylate; and of the action of ethylic sodioacetoacetate on ethylic α-chlorocrotonate.

113. "*Formation of Pyrazolone Derivatives from Chlorofumaric Acid.*" By SIEGFRIED RUHEMANN, Ph.D., M.A.

The author describes the products of the action of hydrazine and phenylhydrazine on ethylic chlorofumarate. In the former case ethylic 5-pyrazolone-3-carboxylate is formed, identical with v. Rothenburg's compound (*J. pr. Chem.,* 1895, li., 53), in the latter an ethereal salt of *bis*-phenylpyrazolonecarboxylic acid. Their properties are described.

114. "*Studies of the Terpenes and Allied Compounds. Note on Ketopinic Acid—a Product of the Oxidation of the Solid Hydrochloride (Chlorocamphydrene) prepared from Pinene.*" By HENRY E. ARMSTRONG.

The acid described has the formula $C_{10}H_{14}O_3$, and is obtained by the interaction of chlorocamphydrene and the strongest nitric acid. It melts at 234° (uncorr.). Baric, calcic, and methylic salts are described, as well as a hydrazone (m. p. 146°) and a hydroxime (m. p. 216°). Ketopinic acid appears to be a saturated ketomonocarboxylic acid.

115. "*Acid Compounds of Natural Yellow Colouring-matters.* Part II." By A. G. PERKIN.

In a previous communication by Perkin and Pate (*Proc.,* 1895, ii., 126), it was shown that when treated with mineral acids in the presence of acetic acid, quercetin, rhamnetin, rhamnazin, fisetin, and morin yielded crystalline compounds, the formula of which is generally represented as an addition product of one molecule of acid to one molecule of colouring-matter. It has since been shown that luteolin and myricetin behave similarly, and there can be little doubt that all these colouring-matters belong to the so-called quercetin group. In this paper certain of these compounds not previously examined are described, viz., quercetin hydrochloride, $C_{15}H_{10}O_7 \cdot HCl$; morin hydriodide, $C_{15}H_{10}O_7 \cdot HI$; and luteolin hydriodide, $C_{15}H_{10}O_6HI$. It is also shown that whereas quercetin tetramethyl ether resembles the monomethyl ether of rhamnetin in reacting with sulphuric acid, and not with the haloid acids, dibromo-quercetin

and tetrabromo-morin yield no compounds with mineral acids. The other known members of the quercetin series are dioxyflavone (Friedländer and Rudt, *Ber.*, 1896, 878) and chrysin, the colouring-matter of poplar buds. The former has been shown by its discoverers to yield acid compounds, but, on examination, the latter was found to be devoid of this property. Various members of the ketone group (gallacetophenone, alizarine, and maclurin), of the xanthone group (gentisin, euxanthone, datiscetin). and of the anthraquinone group, were examined in this respect, but yielded no compounds with mineral acids. Catechin and kinoïn also, the latter a constituent of malabar kino, did not react.

For the constitution of the acid compounds two schemes are put forward, the first a similar one to that suggested by Nietzki and Schröber (*Ber.*, 1895, 50) for the phthaleine salts, and a second depending upon the saturation of the ethylene-bond in the γ-pyrone ring.

It is considered probable that this reaction is characteristic of the quercetin group, and will thus be of service for distinguishing its members from the other classes of non-nitrogenous, yellow, mordant dye stuffs which are at present known to exist.

116. "*Studies on Citrazinic Acid.*" Part IV. By W. J. SELL, M.A.

The author has employed Tiemann and Reimer's reaction (*Ber.*, 1876, ix., 423, 824) to introduce the aldehyde group into hydroxyl derivatives of pyridine, and has isolated and analysed the disodium salt of the mon-aldehyde of citrazinic acid, the monaldehyde acid, the oxime of the monaldehyde acid, and the phenylhydrazine salt of the hydrazone.

117. "*The Action of certain Acidic Oxides on Salts of Hydroxy Acids.*" III. By G. G. HENDERSON, D.Sc., M.A., and JOHN M. BARR.

By the prolonged boiling of antimonious oxide in an aqueous solution of the primary malate, *amnonium anti-monio malate* was obtained,

$$2Sb_2O(C_4H_4O_5NH_4)_4 \cdot Sb_2O(C_4H_5O_5)_4 \cdot 20H_2O,$$
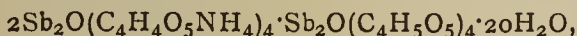
resembling the potassium salt already described (*Trans.*, 1895, 1030). It forms large colourless crystals, easily soluble in water, and decomposes when heated to about 115°, or when its aqueous solution is boiled for a short time, except in presence of excess of the oxide.

Antimonious oxide dissolved slowly in a boiling solution of sodium hydrogen malate, and, on adding alcohol, a syrup was precipitated, which consisted principally of the sodium compound. However, the pure salt could not be obtained in a crystalline condition.

While arsenious oxide dissolved freely in solutions of primary sodium and ammonium malates, salts corresponding to the antimonio-malates could not be prepared in a pure state, owing to the instability of the products, although an impure ammonium compound was obtained.

*Ammonium antimonio-mucate*, SbO(NH₄)C₄H₈O₈·3H₂O, was prepared by prolonged boiling of the oxide with a solution of the primary mucate and repeated re-crystallisation of the product. It is a white, finely crystalline powder, sparingly soluble in cold, but fairly easily soluble in hot water. In its other properties it closely resembles the potassium salt already described (*loc. cit.*). The *sodium salt*, SbONaC₄H₈O₈·3H₂O, prepared similarly, is also a white crystalline powder, only differing from the others in its greater solubility in water. On addition of barium acetate to a solution of the sodium salt, what appeared to be a slightly impure barium salt was gradually precipitated in the form of a white powder.

Attempts to prepare arsenio-mucates of sodium and ammonium were not successful, and failure also attended our efforts to obtain compounds of the alkali salts of mandelic acid with antimonious and arsenious oxides respectively.

Salicylic and gallic acids were then taken as examples of phenol acids, but experiments showed that neither antimonious nor arsenious oxide entered into reaction with any of the alkali salts of these acids.

Molybdenum trioxide was found to dissolve in boiling aqueous solutions of primary tartrates, forming compounds with them. *Sodium molybdi-tartrate*,—

$$MoO_2(NaC_4H_4O_6)_2 \cdot 3H_2O,$$

was obtained in the form of a white crystalline powder, easily soluble in cold water, and decomposed on exposure to light or to a temperature of 90°, and also when its aqueous solution is boiled for some time. The *potassium salt* is also a crystalline powder, very similar in properties to the sodium salt, but less stable. The ammonium salt was only obtained in the form of a gelatinous precipitate.

*Sodium tungsti-tartrate*, WO₂(NaC₄H₄O₆)₂·5H₂O, was prepared by dissolving tungsten trioxide in a boiling aqueous solution of the primary tartrate, excess of the latter being used. It crystallises in white plates, easily soluble in water, and decomposed when heated to about 110°, or when its aqueous solution is boiled for any length of time. The *potassium salt*, WO₂(KC₄H₄O₆)₂·4½H₂O; and the *ammonium salt* are also crystalline, the former closely resembling the sodium salt in properties, the latter being very unstable in presence of water. The *barium salt*, WO₂(C₄H₄O₆)₂Ba, is precipitated as a white insoluble powder when barium acetate is added to a solution of the sodium salt.

Silicon dioxide, used in the form of gelatinous silicic acid, apparently does not react directly with primary tartrates, but titanium dioxide dissolves in solutions of these salts, yielding substances which are being examined. It remains to be tried whether other acidic oxides also react with tartrates and salts of other hydroxy-acids.

118. "*Note on γ-Acetobutyric Acid,*—

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH."$$

By W. H. BENTLEY and W. H. PERKIN, Jun.

The properties of this acid were carefully investigated in order to enable the authors to compare it with a ketonic acid obtained from sulphocamphylic acid. It was prepared by the hydrolysis of ethylic acetyl glutarate (Wolff, *Annalen*, 1883, ccxvi., 129), the method of preparation being improved in some respects.

The oxime (m. p. 104—105°) and the *semicarbazone* (m. p. 174°) are the most characteristic derivatives; when oxidised with nitric acid, aceto-butyric acid yields succinic acid.

119. "*Some Derivatives of Propionic Acid, of Acrylic Acid, and of Glutaric Acid.*" By W. H. PERKIN, jun.

This paper describes in the first place the results of the investigation of *dimethylacrylic acid*,—

$$(CH_3)_2 \cdot C:CH \cdot COOH;$$
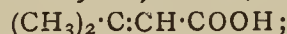
*trimethylacrylic acid*, (CH₃)₂C:C(CH₃)·COOH; and *isopropylacrylic acid*, (CH₃)₂CH·C(:CH₂)·COOH.

The ethereal salt of the former acid, when digested in alcoholic solution with the sodium compound of ethylic malonate, yields *ethylic dimethylpropanetricarboxylate*, (COOC₂H₅)₂CH · C(CH₃)₂ · CH₂ · COOC₂H₅ (compare Auwers, *Ber.*, 1895, xxviii., 1130; *Annalen*, 1896, ccxcii., 145), (b. p. 203°, 60 m.m.), from which, by hydrolysis and elimination of carbon dioxide,—

$$COOH \cdot CH_2 \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH,$$

*ββ-dimethylglutaric acid*, was obtained. This acid melts at 101°, and gives an anhydride melting at 124° and an anilic acid melting at 134°.

*Trimethylacrylic acid*, together with *isopropylacrylic acid*, results from the action of alkalis on *ethylic α-bromo-αββ-trimethylpropionate*,—

$$CH(CH_3)_2 \cdot CBr(CH_3) \cdot COOC_2H_5.$$
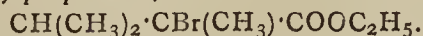
The former is a crystalline compound which melts at 70—71°, and from which the following derivatives have been prepared.

*αβ-Dibromo-αββ-trimethylpropionic acid,*—

$$CBrMe_2 \cdot CBrMe \cdot COOH$$

(m. p. 188°).

*β-Bromo-αββ-trimethylpropionic acid,*—

$$CBr(CH_3)_2 \cdot CH(CH_3)COOH$$

(m. p. 88°).

*β-Iodo-αββ-trimethylpropionic acid,*—

$$CI(CH_3)_2 \cdot CH(CH_3) \cdot COOH$$

(m. p. 88°).

When the mixed ethereal salts of trimethylacrylic and isopropylacrylic acids (as obtained by the action of quinoline on ethylic α-bromotrimethylpropionate) are digested with the sodium compound of ethylic malonate, the ethylic isopropylacrylate only enters into the reaction with formation of *ethylic isopropylpropanetricarboxylate*, $(COOC_2H_5) \cdot CH_2 \cdot CH_2 \cdot C(COOC_2H_5)_2 \cdot CH \cdot (CH_3)_2$ (b. p. 208—210° at 45 m.m.), the ethylic trimethylacrylate remaining apparently unattacked.

$$(COOH) \cdot CH_2 \cdot CH_2 \cdot C(COOH)_2 \cdot CH(CH_3)_2,$$

*isopropylpropanetricarboxylic acid*, crystallises in colourless needles, which melt at 265° with decomposition into carbon dioxide and *isopropylglutaric acid*,—

$$COOH \cdot CH_2 \cdot CH_2 \cdot CH(COOH) \cdot CH(CH_3)_2.$$

This acid melts at 95°, and gives an *anhydride* at 53° and an *anilic acid* melting at 158—159°; its constitution is proved by its synthesis from ethylic isopropylmalonate and ethylic β-iodopropionate.

This paper contains also an account of a number of experiments on the action of phenoxyethylbromide, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Br$, on the sodium compounds of ethylic dimethylpropanetricarboxylate and ethylic isopropylpropanetricarboxylate.

120. "*On the Action of Chloroform and Potash on Metamidobenzoic Acid.*" By W. J. ELLIOTT, M.A.

By the action of aqueous potash and chloroform on metamidobenzoic acid, a compound is obtained which is insoluble in all solvents, reduces Fehling's solution, and gives with phenylhydrazine a red compound, which is not a hydrazone, but has the properties of an azo-compound.

The compound has the empirical formula $C_8H_7NO_3$, and the author suggests the constitutional formula—

$$\begin{array}{ccc} NH_2 & & NH_2 \\ | & & | \\ C_6H_3 \cdot CHOH \cdot CO \cdot C_6H_3 &, & \\ | & & | \\ COOH & & COOH \end{array}$$
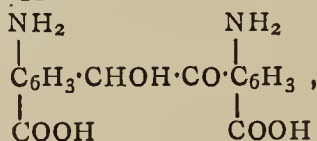
that is di-amido-di-carboxy-benzoin. When boiled with water for some time, the compound is oxidised, yielding a solution of metamidobenzoic acid. With phenylhydrazine, metamidobenzoic acid and a compound having the empirical formula $C_7H_6N_2$, are formed. The author suggests the formation of an osazone, which is reduced, by the hydrogen set free, to metamidobenzoic acid and a disazo-compound of the formula—

$$C_6H_5 \cdot N:N \cdot CH:CH \cdot N:N \cdot C_6H_5.$$

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PHYSICAL SOCIETY.

*Ordinary Meeting, November 13th, 1896.*

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Captain ABNEY, President, in the Chair.

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A PAPER "*On some Experiments with Röntgen's Radiation,*" by Prof. THRELFALL and Mr. POLLOCK, was, in the absence of the authors, read by the Secretary.

The authors describe a form of Crookes's tube which, while it can be made by anyone capable of the most elementary glass-blowing, gives a plentiful supply of Röntgen rays. The results of their experiments may be summed up as follows:—

(1) The Röntgen radiation does not consist in the projection of gaseous matter, or, if it does, the amount of such matter involved is extraordinarily small.

(2) The Röntgen radiation does not consist in the projection of æther streams having a velocity above a couple of hundred metres per second : this is true whether the radiation takes place in air or in benzene.

(3) The properties of the æther, regarded as determining the velocity of electro-magnetic waves, are not greatly changed (*i.e.*, not at all within our experimental limits) by the Röntgen radiation, and this applies alike to the æther in air and in benzene.

(4) A selenium cell, composed of platinum electrodes and highly purified selenium, is affected by Röntgen radiation to an extent which is comparable with the effect produced by diffused daylight.

(5) No permanent or temporary electromotive force is set up in a selenium cell by the Röntgen radiation.

The authors have come to conclusion (1) by exposing an exhausted tube placed in parallel with a spark-gap so adjusted that the spark just passes over the gap rather than through the tube to the Röntgen radiation. They find that a vacuum tube in parallel with a spark-gap is very sensitive to changes in pressure within the tube. Conclusions (2) and (3) were arrived at by using Michelson's arrangements for the interference of two beams of light.

Mr. SHELFORD BIDWELL said he had made some experiments on the effect of Röntgen rays on the resistance of selenium, but with a negative result, although he could have detected a much smaller change than that found by the authors. It might be that this difference was due to the tube, for in his experiment the radiation started from a platinum plate within the tube, while in the authors' arrangement the radiation starts from where the kathode rays strike the glass of the tube.

Prof. SILVANUS THOMPSON said there were a number of points with reference to the Röntgen radiation which required clearing up. For instance the suggestion that they were vortices in the æther had not been tested. Again, Lafay says that if the rays are passed through a metal screen which is charged with electricity, then the rays can be deflected by a magnet. He (Prof. Thompson) had not been able to repeat this experiment, neither had he that of Galitzine on the polarisation of the rays by tourmaline. The statement of Prof. J. J. Thomson, that under the influence of the radiation paraffin became a conductor, had not been satisfactorily proved. As to the wave-length, while some observers obtained values about one-tenth that of the extreme violet, another had obtained a value greater than that of the extreme red. He (the speaker) did not understand the authors' device for detecting changes in the vacuum of a tube, since everyone who has worked with Crookes's tubes has found that the resistance is always greater for a spark in one direction than in the other, and also varies with the battery power employed. Lenard, adopting Hertz's arrangement, uses as anode a cylinder surrounding the kathode (a disc), the idea being that by using such a symmetrical arrangement the kathode radiation was more homogeneous. It might be advisable, when seeking to produce homogeneous Röntgen rays, to adopt such a symmetrical arrangement.

The CHAIRMAN said that since no selection was made with reference to the announcements which appeared in the *Comptes Rendus*, it was frequently found that these announcements turned out to be wrong.

Mr. BRYAN then read a paper, by himself and Dr. BARTON, "*On the Absorption of Electrical Waves along Wires by a Terminal Bridge.*"

The authors employ, for the generation of the oscillations, an arrangement of the same description as that used by Bjerknes, the waves being propagated along two parallel wires about 116 m. long. In order to measure the waves, they use a small electrometer with an uncharged needle. The resistances employed to form the

bridge consist of pencil-marks on ground glass. Bridges of three resistances have been examined, one having as nearly as may be the resistance necessary, according to Heaviside's theory, to give complete extinction of the reflected wave, and of the others one was of higher and the other of lower resistance. In each case the results confirm the theory, and it is thus experimentally proved that, by using a bridge of this description, the reflected train of waves can be completely extinguished.

Mr. BLAKESLEY asked if the authors had made any allowance for the capacity of the wires.

Mr. CAMPBELL asked if the resistances given were expressed in ohms or in electro-magnetic units.

Mr. BIDWELL asked if the authors had found that the pencil-trace resistances obeyed Ohms' law. He found that if you balance with one cell in the battery circuit, then, on increasing the battery power to two cells, the resistance alters.

Mr. APPLEYARD suggested that the variation was caused by the contacts at the ends not being good.

Mr. CAMPBELL said the same variation occurred in the case of mixtures of clay and plumbago where the contacts could be made quite good.

Mr. CARTER suggested electroplating the ends to give good contact.

Mr. BRYAN, in his reply, said that they had not considered the question of capacity, and that in their case they did not require to know the resistance very accurately.

The Society then adjourned till November 27th.

# NOTICES OF BOOKS.

*The Energy of Living Protoplasm.* By OSCAR LOEW, Ph.D., Professor in the Imperial University, Japan. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1896.

THE author has come to the conclusion that there must exist an unstable modification of albumen with which alone we have to do in living protoplasm, and differing from that of dead protoplasm or from ordinary protoplasm, though easily passing into the latter. He declares that the electrical phenomena observed are like animal heat, mere secondary actions and not the first cause of life. He quotes Liebig (*Chemische Briefe*, xxiii., 1858) as defending energetically the doctrine of a specific vital power. Reil, Schleiden, Matteucci, and Lehmann all protest more or less against this vitalistic hypothesis. Tyndall's celebrated dictum that we have in matter the "promise and potency of every form and quality of life" is, it is here pointed out, merely the re-issue of an old thought of Francis Bacon "De princip. atque origg." (*Opera ed. Bohn.*, ii., 691).

We find here honour awarded to a man who is generally overlooked by his own countrymen. We are reminded how Dr. Mayow showed "that life and fire are sustained by one and the same principle contained in the air, and that this principle is mixed with another indifferent substance. He can be considered not only as a forerunner of Lavoisier, but also as the first propounder of the doctrine of the conservation of energy."

But passing over not a few such significant utterances we come to the main passage in which Professor Loew sums up his facts :—

1. The transition of living protoplasm into dead protoplasm exhibits a far-reaching resemblance to the transition of a labile substance into an isomeric stable form of atomic migration.

2. Compounds that easily enter into reaction with aldehyds are poisonous for all kinds of organisms. Such compounds have no action upon dead protoplasm or upon common proteids.

3. Compounds that easily enter into reaction with *labile amido-groups* are poisonous for all kinds of organisms, but these compounds have an action upon ordinary proteids also, and therefore also upon dead protoplasm.

4. There exists widespread in the vegetable kingdom a highly labile proteid serving as reserve material, which undergoes chemical change by the same influences as those which cause the death of the cells.

We are not prepared to say that Dr. Loew's speculations are as yet included among chemical orthodoxies, but they certainly merit a close and candid scrutiny.

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*The Chemical Analysis of Iron.* A Complete Account of all the best known Methods for the Analysis of Iron, Steel, Pig-iron, Iron Ore, Limestone, Slag, Clay Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR, Graduate United States Naval Academy, 1866; Chief Chemist United States Board appointed to test Iron, Steel, and other Metals, 1873; Chief Chemist United States Geological Survey and Tenth Census, 1880; Member American Philosophical Society, &c. Third Edition. Philadelphia: J. B. Lippincott Company. London: 10, Henrietta Street, Covent Garden.

THE vast extent and growing prosperity of the iron manufacture in the United States have naturally drawn the attention of chemists to metallurgy, and especially the metallurgy of iron. The present work is the natural result of these circumstances, and has most admirably met the demand thus created. The author sets out with instructions for the preparation of samples and an account of the apparatus particularly required in the siderurgical laboratory.

It will be noticed that for crucibles pure platinum is recommended in preference to the iridium alloy, which is "much more likely to crack." Mr. Blair recommends the laboratory to be provided with two balances, one for weighing crucibles, &c., and another, much smaller, for weighing out the portion taken for analysis. Then follow the reagents required, with special instructions for preparing magnesia mixture and molybdate solution. We are glad to observe that the former mixture is directed to be prepared from magnesium and ammonium chlorides without any sulphates.

We then come to the analysis of pig-iron, wrought iron, and steel, involving the determination of sulphur, silicon, slag, and oxides, phosphorus (especially in presence of titanium), manganese, carbon (total, graphitic and combined), copper, nickel and cobalt, chromium and aluminium, arsenic, antimony, tin, tungsten, vanadium, and nitrogen.

Then follow procedures for the analysis of iron ores, of limestones, clay, slags, fire-sands, coal, and coke. Next we come to the analysis of the gases, carbonic acid, carbon monoxide, oxygen and hydrogen, and hydrocarbon $CH_4$. Then come certain tables.

For calculating the weight of the substance sought for from that of the substance found, we do not meet here or in any other text-book an arrangement as simple as that to be found in Rose, vol. ii., A. Normandy's version (Tegg and Co., 1849).

Blair's work will be found most valuable by all chemists connected with the iron trade.

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*Catalogue of Case School of Applied Science*, Cleveland, Ohio. 1895-96. Cleveland: J. B. Savage.

THIS pamphlet is of no small interest, as it affords us the opportunity of comparing two very distinct systems of higher education; to wit, that prevailing in the United States, and that almost universally established on the European continent. In Europe, Britain always

excepted, all colleges and universities are under the direct and close superintendence of the State. In America, on the contrary, free scope is given to private enterprise. Universities, colleges, schools of science—such as the one described in the publication before us,—may be founded and endowed by any private individual, syndicate, or religious denomination, and may obtain legal incorporation and the power to grant degrees which are officially recognised. The position corresponding to the *Senatus Academicus* is held by a body of trustees. The "courses," or, as they would be called in Germany, "faculties" are in the Case School civil engineering, mechanical engineering, electrical engineering, mining engineering, physics, chemistry, architecture, and general science. The degrees which may be awarded are those of "Bachelor of Science" and "Master of Science." These degrees cannot be obtained without the production of a thesis showing actual work in one or other department. The expense of the course is stated to be from 275 to 350 dollars for tuition, board, room, books, &c., per annum. Among the subjects taught we notice "economics," "civics," and rhetoric, three subjects of little value to the men of science, but priceless to the politician and the agitator. It seems to us that upon some, at least, of the professors is thrown a mass of incongruous work. Thus, Professor Comstock undertakes rhetoric, English, composition, descriptive geometry, biology, in the departments of zoology and botany and geology. If he can teach all these subjects *con amore* he must be something more than an admirable Crichton. The work must be the harder because the botany, zoology, and geology are to be taught not merely from books but in the laboratory. What are the "recitations" mentioned as taking up much of the morning hours? We hope not committing text-book to memory. We are watching the career of the American science schools with the more interest as some of them are now producing good work.

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*A New Course of Experimental Chemistry, Including the Principles of Qualitative and Quantitative Analysis;* Being a Systematic Series of Experiments and Problems for the Laboratory and Class Room. By JOHN CASTELL-EVANS, F.I.C., Senior Demonstrator and Lecturer on Chemistry at the City and Guilds of London Institute's Technical College, Finsbury. London: Thomas Murby, Pp. 244.

WE have been able on a former occasion to congratulate Prof. Castell-Evans on his method of teaching chemistry. He does not lay before his pupils the facts and laws of the science to be read over or "memorised." But he guides them into ascertaining such facts and principles for themselves by a well selected course of experiments. For the performance of these experiments he gives excellent advice. The student who has worked through the problems here laid down in a conscientious and intelligent manner will be worth calling a chemist. Whether he will be able to "pass exams." we do not presume to foretell, but he will certainly be able to take up unsolved questions, theoretical or practical, and to throw a new light upon them.

We much regret, however, to find the author advocating needless complication as regards the denominations of the metric system of weights and measures. We all know that French chemists express the cubic centimetre in the singular or plural number by the abridgement *c.c.*, and that we in this country do the same.

Such abbreviations are perhaps too simple for the Teutonic mind, and we accordingly find German authors, with the signal exception of Prof. Fresenius, writing *c.c.m.* or *c.c.m.s.* Mr. Castell Evans appears to follow their example. Yet he retains the sensible abridgement *m.m.* for millimetre.

In all other respects, as far as we have been able to trace, the author's precepts and example are alike worthy of being followed.

The "Introductory Remarks" are a perfect mine of precious truth. Thus we read "on no account is he (the student) to be permitted to perform mental gymnastics or conjure with symbols and formulæ." The author speaks of the prospect of chemistry being "raised to the dignity of a deductive science." Such a "rise" would in some senses be small benefit.

Upon the whole Mr. Castell-Evans' method of teaching deserves very general adoption.

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*Chemical Lecture Experiments.—Non-Metallic Elements.* By G. S. NEWTH, F.I.C., F.C.S., Chemical Lecture Demonstrator at the Royal College of Science, South Kensington. London, New York, and Bombay: Longmans, Green, and Co. New and Enlarged Edition. Pp. 344, Crown 8vo. 1896.

THE author's object has been to supply lecturers and teachers with a store of experiments illustrative of the preparation and the properties of the non-metallic elements. The instructions given are full and clear, none of them having been introduced at hearsay, or copied from other books or documents. The author has omitted all dangerous experiments.

Though using the metrical system of measurement, he has given the English equivalents of the French measures of length, justly remarking that, though the British scientific mind has acquired the habit of thinking in grms. and c.c., it still conceives of measures of length in inches. Sources of danger are pointed out where they may occur.

The illustrations are not only numerous and to the purpose, but very correctly and clearly drawn.

Not merely the teacher but the student will find this work very useful, as it will often save him the trouble of sketching the apparatus which he sees in use on the lecture table. Hence Mr. Newth's work will prove a valuable companion to any text-book of the chemistry of the non-metallic elements and their compounds.

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*University College of North Wales, Calendar for the Year* 1896-7. Manchester: J. E. Cornish.

WE have here a full prospectus of the North Wales University College, and are glad to recognise what are, in our opinion, steps in the right direction. Thus, if we do not misunderstand this calendar it will be open practically for a student to proceed to the degree *Baccalaureus in Scientia* without any course of study in classics. The "departments" of studies seem essentially to correspond to the distinct faculties in the Continental Universities. Chemistry, physics, and biology seem to receive an approximately fair share of attention, and special laboratories are devoted for their study. There are rooms for photography, for gas analysis and for spectroscopic work, a physical and a chemical lecture theatre, a chemical museum, an optical room, a room for electrical measurements, biological laboratories and lecture theatres (botanical and zoological). A very important feature is the agricultural department. In short, as far as we can judge from a careful examination of the descriptions and plans of the laboratories, there is here scope for genuine work in the sciences concerned.

A fact showing that the authorities of the College really "mean business" is that the chemical and physical departments were opened in February, 1885, by Lord Kelvin, with an appropriate address. We trust that the College will make good use of the facilities placed at its disposal.

Should there not be a special mining and metallurgical department?

# CORRESPONDENCE.

## ACTION OF THE METALS AND THEIR SALTS ON THE ORDINARY AND ON THE RÖNTGEN RAYS.

*To the Editor of the Chemical News.*

SIR,—In an interesting paper on the above subject, communicated to the British Association in September, by Messrs. Gladstone and Hibbert, and fully reported in the CHEMICAL NEWS (lxxiv., 235), reference is made to the first workers in this field, who are specially mentioned by name. The authors omit the names of W. Ackroyd and H. B. Knowles, who, in a joint paper to the Physical Society of London, clearly showed by a photograph submitted to a Meeting on March 13th, and which had been taken on the previous 20th February, that "selective absorption of the X rays is a function of the atomic or molecular weight." These experimenters were the first in England to enunciate the fact, and the results of any foreign work were not as yet to hand.

In the writer's little work on "The Old Light and the New" (Chapman and Hall), published in April, the law is shown to hold for the elements in the periodic groups I., II., IV., V., and VIII. See pp. 73—80 in a copy forwarded.—I am, &c.,

WM. ACKROYD.

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## ESTIMATION OF SULPHUR IN CAST-IRON OR STEEL.

*To the Editor of the Chemical News.*

SIR,—As regards the method described by G. G. Boucher (CHEMICAL NEWS, lxxiv., p. 74) I would point out that it is not new; as, in the *Journal of the Iron and Steel Institute* (1888, Part II.) there appears an abstract of an article, by C. Meincke, in which practically the same method is given for the determination of sulphur in pig-iron and spiegeleisen.—I am, &c.,

J. JAS. MORGAN.

10, Bryntirion Street, Dowlais.
Nov. 13, 1896.

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**Society of Arts.**—The first course of Cantor Lectures at the Society of Arts will be by Professor Vivian B. Lewes, on "The Use of Gas for Domestic Lighting." The subjects dealt with include :— The principles of illumination and the measurement of light ; flat flame, Argand, and regenerative burners ; incandescent mantles and burners; the effect of globes in diffusing and absorbing light ; atmospheric influences and the penetration of light ; gaseous illumination where coal-gas is not available ; oil-gas and its properties ; acetylene, its manufacture and use. The course commences on Monday, the 23rd inst., and will be continued on the two following Mondays.

**Determination of Volume of Pulverulent Bodies by Shaking.**—Gluckmann (*Pharm. Central Halle*).—A cylindrical measure, 20 c.m. in height and $2\frac{1}{2}$ c.m. in diameter, graduated in c.c. from its flat bottom upwards, is charged with the powder in question and then knocked upon a support (not too hard) until there occurs no further decrease in volume. If the volume is then divided by the weight of the quantity of substance used we obtain a value which the author names relative volume.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Parts 4 and 5.

**The Chemical Examination of Cheese.**—A. Stutzer. —The author determines the ash and its constituents, employing a platinum capsule in a muffle furnace. For the other determinations a considerable quantity of the cheese is well rubbed up with quartz sand, previously washed, ignited, and sifted, the proportion taken being 100 grms. cheese to 400 grms. of sand. The total nitrogen is estimated by the Kjeldahl method. Cupric hydroxide is an unsuitable precipitant for the albumenoids if they are mixed with pancreas-peptone. The author uses phosphotungstic acid for separating the valuable caseines and albuminates, and their first scission products (including the albumoses and pancreas-peptones), from the worthless decomposition products, such as phenylamido, propionic acid, tyrosin, leucin, and other amides. IV. The nitrogen present in the state of ammoniacal salts is estimated by distillation with barium carbonate. V. Nitrogen in the state of amides is found as the nitrogen of compounds not perceptible by phosphotungstic acid and not belonging to ammonia. VI. The indigestible nitrogenous matter is found as the residue not acted on by rennet. VII. The determination of nitrogen existing as albumose and peptones. VIII. The caseins and albuminates are found by deducting from the total nitrogen the nitrogen not precipitable by phosphotungstic acid (V.), the indigestible nitrogen (VI.), and the nitrogen existing as albumose and peptone (VII.).

**The Examination of Commercial Thorium Nitrates and the Separation of Ceria and Thoria.**—R. Fresenius and E. Hintz.—This paper will be inserted in full.

**Prevention of Corrosive Liquids being Drawn into the Mouth when filling Pipettes.**—F. F. Skinner (CHEMICAL NEWS).

**Regulating Cock for adjusting Temperature in Distillation, Desiccation, &c.**—G. Hansdorff (*Zeit. f. Angewandte Chemie*).—On the plug of the glass cock is fixed a one-armed lever with a circular scale.

**Iron Wire Nets with Asbestos Covers.**—Sohniewindt (*Zeit. Ange. Chemie*). — The author pronounces such nets little inferior to metal gauze.

**A Modification of the Litre Flask.** — W. M. B. Giles (CHEMICAL NEWS).

**An Analytical Funnel.** — R. Muencke. — Shown in an accompanying figure.

**A Celluloid Funnel.** — A. H. Edwards (CHEMICAL NEWS.

**Gas-generators, especially for Sulphuretted Hydrogen**—J. F. Liversidge.—From the CHEMICAL NEWS.

**Bunsen Burner, with a Safety-basket of Wire-netting.**—(Joint-Stock Co. for water-leads and installations for lighting and heating).—On the principle of the Davy safety-lamp.

**Substitute for the Chemical Balance.**—H. Joshua Phillips (CHEM. NEWS).

**Modification of the Nitrometer.** — Emile Henry (*Bull. de la Soc. Chim. de Paris*).

**Apparatus for Drying and Absorbing Gases in Elementary Analysis.** — James Leicester. — From the CHEMICAL NEWS.

**Refrigerator for Distillations from a Test-glass.**— C. J. Brooks.—From the CHEMICAL NEWS.

**Hot-water Funnel.**—C. R. Beck (CHEMICAL NEWS).

Volatilisation of Salts during the Evaporation of Water. — G. H. Bailey. — From the *Journal of the Chemical Society*.

Expansion of Water on Change of Temperature.— Stephane de Lannoy.—From *Comptes Rendus*, cxx., 866.

New Method of Quantitative Spectral Analysis.— G. and H. Krüss.

Direct Spectroscopic Examination of Minerals and of some Fused Salts.—A. de Gramont.—From *Comptes Rendus*, cxxi., p. 121.

Separation of three Liquids by Fractionated Distillation.—F. R. Barrell, G. L. Thomas, and Sydney Young.—From the CHEMICAL NEWS.

Measurement of High Temperatures, especially of the Melting-points of some Inorganic Salts.—John McCrae (*Annalen der Physik und Chemie*).—Already noticed.

Determination of Fusion and Ignition Points.— W. R. Hodgkinson.—From the CHEMICAL NEWS.

Heating by Electricity.—L. C. Levoir.—From the CHEMICAL NEWS.

Loosening Glass Stoppers.—R. W. Hill.—From the CHEMICAL NEWS.

∴ Cleansing Port-Objects from Oil, Canada Balsam, &c.—Zettnow (*Central Blatt fur Bakteriologie*).—The author steeps covering-glasses in oil of turpentine, then boils in hydrochloric acid and potassium chlorate. Finally the glasses are heated in a paste of powdered steatite, sawdust, soda, and water, rinsed in hot water, in water containing hydrochloric and acetic acids, and finally rinsed with alcohol.

Normal Barometer for the Laboratory.—K. R. Koch (*Annalen der Physik und Chemie*).—A syphon barometer with an upper and lower expansion, into each of which is fused a thermometer graduated into tenths of a degree. In connection with the barometer is a distillatory globe from which fresh mercury can be distilled into the apparatus. A Crookes tube is also connected with the apparatus to test the vacuum.

A Consistency Meter.—Weiss.—A patented device, which cannot well be described without the aid of illustrations.

Construction of the Slit of Spectroscopes.—W. Crookes.—From the CHEMICAL NEWS.

A Dephlegmator.—Sydney Young and E. L. Thomas. —From the CHEMICAL NEWS.

Taking Samples of Water for Bacteriological Purposes.—W. T. Burgess.—From the CHEMICAL NEWS.

Extraction Apparatus.—L. L. de Koninck (*Chemiker Zeitung*).—This paper requires the accompanying figures.

Apparatus for Extracting Soluble Phosphoric Acid from Superphosphates.—W. D. Horne.—From the CHEMICAL NEWS.

Revolver Pipette.—A. Stutzer (*Zeit. Angew. Chemie*). —The lower end is provided with a two-way cock.

## MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Society of Arts, 8. " The Use of Gas for Domestic Purposes " (Cantor Lectures), by Prof. Vivian B. Lewes.
WEDNESDAY, 25th.—Society of Arts, 8. " Recent Developments in Mechanical Road Carriages," by J. Worby Beaumont, M.Inst.C.E.
FRIDAY, 27th.—Physical Society, 5. "Apparatus for giving Diagrams of the Efficiency of a Photographic Shutter," by Captain Abney, F.R.S.

## TO CORRESPONDENTS.

*Atom.*—The fee would vary considerably, according to the school or college selected. Consult our " Students' Number."

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1931.

## THE ALLEGED NEW ELEMENT, LUCIUM.

### By WILLIAM CROOKES, F.R.S.

THROUGH the kindness of M. P. Barrière, the patentee of Lucium, I have been placed in possession of a solution of lucium nitrate, and a larger quantity of precipitated oxalate, both said to be tolerably pure. I have thus been enabled to try a sufficient number of experiments to convince me that the claim of lucium to form one of the chemical elements is not justified.

Preliminary examination with a hand spectroscope showed the presence of didymium and erbium in small quantities. The nitrate solution was evaporated to dryness and ignited. It left a cream-coloured earth, easily soluble in dilute nitric acid. The oxalate on ignition gave an earth having similar properties.

Radiant matter tests were made of the original earth. It phosphoresced very well when submitted to the induction current in a vacuum tube, and the spectrum of the emitted light was that of yttria. All the lines and bands were there, but they were deficient in sharpness, showing the presence of impurities.

A larger quantity of oxalate was converted into nitrate and evaporated to dryness and submitted to fractionation by partial decomposition by fusion. Five operations in all were performed, and similar radiant matter tests were performed on the two extremes and on the centre earth. All showed the yttrium phosphorescent spectrum. The fusing nitrates required a high temperature for decomposition, like yttrium nitrate; the extremity at the + end was in consequence larger than that at the − end. On the + side the didymium bands in the absorption spectrum gained in intensity, while on the − side they were very faint.

Portions of the earths from each fraction were converted into sulphates, ignited, and tested in the radiant matter tube. The result showed that the removal of the more easily decomposable nitrates from the fraction at the + end brought out the sharpness and brightness of the yttria bands, this fraction phosphorescing almost like pure yttria. A similar radiant matter test on the extreme fraction at the − end gave a poor yttria spectrum, the erbium phosphorescent spectrum being also visible.

Photographs were taken of the ultra-violet spectrum of lucium. The spectrograph has a complete quartz train, and the pictures were taken on films curved to the proper curvature to get all the lines in focus at once. The nitrate in strong solution was put into an appropriate tube, and sparks from a large induction coil, having a jar intercalated, were passed between the solution and a platinum pole; a very short spark being employed. The lines in the lucium spectrum closely resemble those in the yttrium spectrum. Spectra were taken of lucium and yttrium, partially superposed so as to detect close coincidences, and on examining several hundreds of lines only six in the lucium spectrum were seen to have no counterpart in the yttrium spectrum. To make certain that I was working with pure yttrium, I used three specimens of the earth and with each I took superposed spectra of lucium: yttria prepared by Clève, called by him "purissimum"; yttria prepared by Marignac, and called by him quite pure; yttria prepared by myself, as pure as I could make it.

To ascertain the absence or presence of other bodies, I compared the lucium spectrum with spark spectra of the following earths, as pure as I could prepare them:—Yttrium, erbium, ytterbium, scandium, thulium, holmium, thorium, didymium, lanthanum, zirconium, glucinum, aluminium, and calcium. In most cases the spectra of lucium and the earth under comparison were photographed partly superposed on the same plate.

Of the six lines unaccounted for, four of them are extremely faint and belong to platinum or air. The fifth line is also faint and is due to a trace of zirconium. The sixth line is strong, and is coincident with a strong line in the ytterbium spectrum.

Spectrum analysis along two different directions shows, therefore, the so-called lucia to be nothing more than yttria in a rather impure condition.

By the kindness of M. Schützenberger, I have received details of the chemical operations through which the monazite passed to separate the lucia from it. They do not materially differ from those given in the patent reprinted in the CHEMICAL NEWS.* The material part of the preparation is the use of sodium thiosulphate, which is said to precipitate lucium and not yttrium. Knowing from long experience the incompleteness of this reagent in separating bodies, I tried the following experiments :—

1. A solution of pure neutral nitrate of yttrium was mixed with a concentrated solution of thiosulphate of sodium, and the action started by heat. As soon as the boiling-point was reached, a slight precipitate was formed, and the liquid was allowed to cool. (In this operation I followed strictly the directions in the patent for separating lucium from yttrium—the lucium precipitating and the yttrium remaining in solution). The precipitate was filtered off and the solution precipitated with ammonia. It was by far the larger quantity of the two.

The small quantity of earth precipitated by sodium thiosulphate was tested in a radiant matter tube and gave the phosphorescent spectrum of yttria. The earth precipitated from the thiosulphate solution was likewise tested in a radiant matter tube and gave also the phosphorescent spectrum of yttria.

Spark spectra were photographed from each of these earths, with the result that they equally showed the lines belonging to yttrium, with no admixture of other lines.

2. Some nitrate of lucium, prepared from M. Barrière's oxalate of lucium, was put through exactly the same treatment to which I submitted the pure yttria in Expt. 1. As in the former case, sodium thiosulphate split it into two portions, the smaller being precipitated and the larger remaining in solution. These two portions were then tested in the radiant matter tube and with the spark, with the result that they each gave an yttria spectrum.

3. A mineral closely allied to monazite, containing a mixture of rare earths, was treated according to M. Barrière's patent, and a small quantity of an earth was obtained which had been separated from the bulk of the yttria present by precipitation with sodium thiosulphate. This was tested by the two spectrum methods and was found to be yttria.

Chemical examination, therefore, confirms the results obtained by spectrum observations, that lucium is nothing but impure yttrium. The error has arisen by considering the sodium thiosulphate separation as a complete one; whereas yttria partially comes down if the solutions are strong and heated.

Too much weight is attached to the fact of the atomic weight of lucium being 104, that of yttrium being 89. The following are the usually accepted atomic weights of the associated earths which may possibly be present :—

| | | | | |
|---|---|---|---|---|
| Scandium | .. | .. | .. | 44·5 |
| Yttrium | .. | .. | .. | 89·0 |
| Didymium | .. | .. | .. | 142·0 |
| Samarium | .. | .. | .. | 250·0 |
| Erbium | .. | .. | .. | 166·0 |
| Ytterbium | .. | .. | .. | 173·0 |
| Thorium | .. | .. | .. | 233·6 |

Considering that didymium and erbium can be detected in the lucium sent me by their absorption bands, and

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* No. 1927, October 30th, 1896.

that ytterbium is shown to be present by a strong line in the spark spectrum, it is not surprising that the presence of bodies of such high atomic weights should raise the atomic weight from 89 to 104.

## ARGON AND HELIUM.

### By Lord RAYLEIGH, F.R.S.

IN his discussion of the probable character of argon and helium, Dr. Brauner (CHEMICAL NEWS, vol. lxxiv., p. 223) seems to leave out of account the evidence derived from the refractivities of the gases. The refractivity of argon is certainly less than that of nitrogen, and the refractivity of helium is much less than that of hydrogen (*Proc. Roy. Soc.*, Jan., 1896); so that, according to the view he favours, $N_3$ is less refractive than $N_2$, and $H_4$ than $H_2$. Is this credible?

Dr. Brauner expects important imformation from determinations of specific heat. Doubtless they will be interesting, but I see no reason to anticipate that the results will differ sensibly from the numbers now available calculated from the laws of thermodynamics. The *ratio* of the specific heats is already known, and by Mayer's principle their *difference* is readily expressed (see, for example, " Theory of Sound," § 246). From the ratio and the difference both values follow, and that without any special molecular hypotheses.

November 20, 1896.

## EXPLANATION OF THE RÖNTGEN RAYS.
### By Dr. T. L. PHIPSON.

FROM all experiments made up to the present time I have come to the following conclusions :—

1. They exist in sunlight, as shown in my note in the CHEMICAL NEWS (vol. lxxiii., p. 223).

2. They exist in the lower part of the spectrum :—

White light ( Prism of ) Heat rays (ultra-red).
    or   { organic } Light rays (colour).
  sunlight ( matter ) Electric rays (ultra-violet, actinic, or X rays).

3. They traverse all organic substances, but are more or less arrested by mineral substances, because all the latter contain a metal, and metals being good conductors they run over the metal.

4. They discharge electrified bodies, because they are electric rays and supply the contrary electricity.

5. They act on the photographic plate, as a galvanic current acts on salts, &c.

6. They emanate from various phosphorescent or fluorescent substances.

The Casa Mia Laboratory, Putney,
    November 20, 1896.

## SUCCESSION OF THE ATOMIC WEIGHTS OF SIMPLE SUBSTANCES.

### By M. DELAUNEY.

I HAVE used in this study the tables of atomic weights given by MM. Mendeleeff and Lothar Meyer, and by the " Annuaire du Bureau des Longitudes." For the values of atomic weights of the simple bodies I have taken the whole numbers which approach nearest to the numbers in the tables.

I have divided the atomic weights thus rectified into

four classes, according as they are multiples of 4 or multiples of the same number + 1, 2, or 3.

*First Class.—Atomic Weights Multiples of 4.*

The atomic weights which are multiples of 4 are contained in the following table :—

| | | | |
|---|---|---|---|
| 12 | Carbon | 124 | Antimony |
| 16 | Oxygen | 128 | ,, |
| 24 | Magnesium | 132 | Cæsium |
| 28 | Silicon | 136 | ,, |
| 32 | Sulphur | 160 | Gadolinium |
| 40 | Calcium | 172 | ,, |
| 44 | Scandium | 176 | Ytterbium |
| 48 | Titanium | 184 | Tungsten |
| 52 | Chromium | 188 | ,, |
| 56 | Iron | 192 | Iridium |
| 80 | Bromine | 200 | Mercury |
| 92 | Cerium | 204 | Thallium |
| 96 | Molybdenum | 208 | Bismuth |
| 104 | Rhodium | 212 | ,, |
| 108 | Silver | 216 | ,, |
| 112 | Cadmium | 240 | Uranium |
| 120 | Antimony | | |

It is to be remarked that the numbers entered in this table are obtained in the same manner in each column by adding successively, setting out from the head of each column, the numbers 4, 8, 4, 4, 8, 4, 4, 4, 4, 24. The head of the first column being 12, the two others follow from 80 to 80.

The table presents gaps due probably to simple bodies as yet unknown, or to atomic weights badly determined.

*Second Class.—Atomic Weights Multiples of 4 + 3.*

The atomic weights of the second class appear to follow the same succession as those of the first, but setting out from 7 instead of 12. This table has only two columns.

| | | | |
|---|---|---|---|
| 7 | Lithium | 87 | Strontium |
| 11 | Boron | 91 | ,, |
| 19 | Fluorine | 99 | ,, |
| 23 | Sodium | 103 | Ruthenium |
| 27 | Aluminium | 107 | ,, |
| 35 | Chlorine | 115 | ,, |
| 39 | Potassium | 119 | ,, |
| 43 | ,, | 123 | ,, |
| 47 | ,, | 127 | Iodine |
| 51 | Vanadium | 131 | ,, |
| 75 | Arsenic | 155 | ,, |

We observe that certain bodies whose atomic weights are multiples of 4 + 3 do not figure in this table. These are—Phosphorus (31), manganese (55), cobalt and nickel (59), copper (63), selenium (79), lanthanum (138), thulium (171), osmium (195), lead (207), thorium (231). On the other hand, we find in the table numerous gaps. Now, these latter seem to correspond to elements which, not being able to subsist, have been decomposed each into two others, whose absence we have pointed out. We have, in fact :—

$2 \times 43 = 31$ (P)     $+ 55$ (Mn)
$2 \times 47 = 31$ (P)     $+ 63$ (Cu)
$2 \times 91 = 79$ (Se)    $+103$ (Ru)
$2 \times 99 = 59$ (Co or Ni)   $+139$ (La)
$2 \times 107 = 7$ (Li)    $+207$ Pb $= 19$ (F) $+195$ (Os)
$2 \times 115 = 59$ (Co or Ni)   $+171$ (Thul)
$2 \times 119 = 7$ (Li)    $+231$ (Th)

*Third Class.—Atomic Weights Multiples of 4 + 2.*

The atomic weights of the third class are few in number. They are :—

| | | | |
|---|---|---|---|
| 2 | Helium | 106 | Palladium |
| 14 | Nitrogen | 126 | Tellurium |
| 70 | Gallium | 182 | Tantalum |
| 90 | Yttrium or Zirconium | 194 | Palladium |

These atomic weights are obtained by setting out from 2 and adding successively 12, 56, 20, 16, 20, 56, 12; numbers which present a remarkable symmetry.

*Fourth Class.—Atomic Weights being Multiples of 4 + 1.*

The atomic weights of this class are, again, less numerous than those of the former groups, but they appear to follow an analogous law.

| | | | |
|---|---|---|---|
| 9 | Glucinium | 101 | Rubidium |
| 65 | Zinc | 121 | ,, |
| 85 | Rubidium | 177 | ,, |

Barium (137), which belongs to the fourth class, seems to be produced by the decomposition of the unstable elementary body 101, as it has been already indicated for the second class. We have, in fact,—

$$2 \times 101 = 65 \text{ (zinc)} + 167 \text{ (barium)}.$$

N.B.—A certain number of simple bodies are not mentioned in any of the four classes above mentioned. There are some bodies as yet little known, such as argon, holmium, neodymium, praseodymium, and terbium; then such bodies as didymium, iridium, and niobium, the atomic weights of which are not established; and, lastly, tin and gold. For tin we hesitate between 117.35 and 118, and for gold between 196.2, 196.6, and 199.

A better knowledge of the atomic weights of the above bodies seems as if it should cause these exceptions to disappear.—*Comptes Rendus*, cxxiii., p. 600.

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## PROXIMATE CONSTITUENTS OF COAL.*

ACCORDING to Baltzer (*Vierteljahrsschr. d. Zür. Naturf.-Gesellsch.*, 1872; also Muck, *Chem d. Steink.*, p. 141) coals are mixtures of complex carbon compounds, these forming a genetic and possibly a homologous series. The framework of carbon contained in these compounds is a complex one, the only analogy to which is that presented by the aromatic compounds. The physical properties of coals are such as to render a classification possible, and these different varieties exhibit a similarity in their ultimate composition. Whilst these several varieties form the essential constituents of coal, there are in addition certain accessory constituents, such as the resinous components, the hygroscopic water, and the "enclosed gases."

The researches of J. W. Thomas, of E. von Meyer, of Schondorff, of Bedson and McConnell, and others, have provided an extensive knowledge of the nature of the gases enclosed in coals from different sources, and also a knowledge of the conditions under which these gases are retained by the coal. The hygroscopic water and the absorptive power for water of different coals have, by reason of their technical importance, received considerable attention.

The remaining group of accessory constituents represented by the resinous bodies, which are distinguished from the coal substance by their solubility, consists of some few hydrocarbons, such as ozokerit, and bodies containing carbon, hydrogen, and oxygen, of which Muck, in his "Chemie der Steinkohle," gives the following:—i. Middletonite; ii. Pyroretinite; iii. Reussinite; iv. Scleretinite; v. Rosthornite; vi. Anthrakoxen; vii. Guayaquillite; viii. Berengelite.

These mineral substances are of varying solubilities in alcohol, ether, and turpentine. From the description given by the different investigators it would appear probable that several of these substances are mixtures.

In 1874 Dondorff drew attention to the occurrence in several Westphalian gas coals of a blackish solid, with a reddish brown colour in reflected light, having a brown streak. This substance is found in thin leaflets on this coal, and is almost entirely soluble in ether, forming a light yellow solution, which fluoresces not unlike solutions of the salts of quinine.

By the extraction of a Westphalian gas coal with ether, Muck has obtained an ethereal solution of a similar character, and from it obtained a solid of the following percentage composition:—

$C = 87.22$, $H = 9.20$, $O = 2.29$, $S = 1.29$ (nitrogen absent). This substance, when heated in a platinum crucible, leaves a coke-like residue amounting to 32.09 per cent. The author considers this substance to be widely diffused in coal, and has shown it to exist in varying amounts in different parts of the same seam. Associated with this investigation is that of P. Siepmann, who has submitted the gas coal of the Pluto mine, Westphalia, to a systematic extraction with chloroform, ether, and alcohol, obtaining the following results:—

The chloroform extract amounted to 1.25 per cent of the coal; the solution, dark yellow to brown in colour, possessed a strong green fluorescence; the composition of the extract was—

$C = 83.46$, $H = 7.93$, $O = 4.27$, $N = 2.71$, $S = 1.63$.

The residue, after extraction with chloroform, gave, when treated with ether, a light yellow solution, having a bluish green fluorescence, from which a solid was obtained amounting to 0.3 per cent of the coal, and containing—

$C = 84.82$, $H = 10.51$, and $O = 4.67$.

The residue, treated with alcohol, gave a solution similar in character to the ethereal solution. The amount removed by the alcohol was 0.25 per cent of the coal, and the composition of the dissolved solid was found to be—

$C = 72.52$, $H = 10.08$, $O = 17.4$.

After the above treatment the residual coal was again extracted with chloroform, which removed 0.75 per cent of the coal, and left on evaporation a dark brown, pitch-like mass, which gave the following results on analysis:—

$C = 78.82$, $H = 8.56$, $O = 9.97$, N (trace), $S = 2.65$.

The last chloroform solution was dark brown in colour and feebly fluorescent.

The composition of the coal before and after this treatment is given below:—

| | C. | H. | O. | N. |
|---|---|---|---|---|
| Before treatment.. | 80.31 | 5.50 | 12.94 | 1.25 |
| After treatment .. | 74.00 | 4.77 | 20.09 | 1.14 |

According to H. Reinsch, alcohol extracts from coal a substance supposed to be altered "chenopodin," a body which the author had discovered in the sap of *Melilotus albus*, and to which he attributes the composition $C_{12}H_{13}O_8N$. In 1885 P. Reinsch concluded that coal consists of two classes of substances, one soluble in alkalis, forming coloured solutions, and a second insoluble.

By the use of phenol as a solvent E. Guignet has extracted from 2 to 4 per cent of a brown solid from coal, which is precipitated from the solution by alcohol. The finely-powdered coal, treated with nitric acid, yields solutions containing oxalic acid and trinitroresorcinol; the insoluble residue contains apparently nitro-compounds, or bodies similar to nitro-cellulose. A portion of this residue is dissolved by caustic alkalis and ammonia, forming brown-coloured solutions.

Guignet, led by the formation of trinitroresorcinol, as mentioned above, attempted to obtain resorcinol by fusion of the coal with caustic soda and distillation in a bath of molten lead, but obtained ammonia and aniline only. The residue after this treatment was, however,

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* Report of the Committee, consisting of Sir I. Lowthian Bell (Chairman), Professor P. Phillips Bedson (Secretary), Professor F. Clowes, Dr. Ludwig Mond, Professor Vivian B. Lewes, Professor E. Hull, Mr. J. W. Thomas, and Mr. H. Bauerman. Read before the British Association (Section B), Liverpool Meeting, 1896.

found to be partially dissolved by water, forming dark brown solutions, from which acids precipitated out humus-like substances. Guignet concludes these bodies are derived from the cellulose residues of the coal, and that the trinitroresorcinol owes its origin to the resinous and wax-like constituents.

During the Session 1889-90 Mr. Saville Shaw, Lecturer in Chemistry at the Durham College of Science, Newcastle-upon-Tyne, made some experiments on the action of a mixture of concentrated sulphuric and nitric acids on bituminous coal. The coal, in a finely-powdered condition, was allowed to remain for three weeks in contact with the mixed acids, and then poured into a large volume of water, filtered, and thoroughly washed. The dried residue differs but slightly in appearance from the original coal, but had evidently undergone change in composition, as after this treatment it gave as much as 77 per cent of "volatile matter," whereas the coal contained but 27 per cent; further, when heated in a test-tube it "puffs" with slight flame, resembling in this respect gun-cotton. A considerable proportion of this "nitro-coal" is soluble in caustic alkalies, yielding very dark brown solutions, from which on acidifying bulky dark brown precipitates are formed. The precipitates, washed and dried, form brilliantly black friable masses, which have not the semi-explosive properties of the original "nitro-coal." Methyl alcohol dissolves some 11 per cent of the nitro-coal, the solution yielding a black scaly product on evaporation, which when heated suddenly decomposes, leaving a very bulky residue of carbon. Attempts to prepare reduction products from this "nitro-coal" were unsucccessful.

In a note published in the *Proceedings of the Chemical Society* (1891-92, p. 9), R. J. Friswell described results obtained by treating finely-powdered coal with dilute nitric acid; a considerable portion of the coal is thus converted into a black insoluble acid, which behaves very much like a "nitro-compound."

Mention should also be made of the investigations of Mr. Watson Smith, published in 1891, on the soluble and resinoid constituents of bituminous coal. The soluble material extracted by benzene from a Japanese coal Mr. Watson Smith has shown to contain phenols, nitrogenous organic bases, and also some aromatic hydrocarbons.

In a previous report experiments with various solvents on a bituminous coal, from the Hutton seam in the county of Durham, were referred to, but, owing to the small yields obtained, this method of attacking the problem as to the nature of the proximate constituents of coal has been relinquished.

The oxidation of the finely-powdered coal with aqueous solutions of potassium permanganate, in some cases made alkaline with caustic potash, appeared to offer a more promising method of attack. The coal uses up very considerable quantities of the permanganate, and dark brown solutions are obtained. From these solutions it has been attempted, by the aid of the formation of insoluble salts, to isolate some of the acids which result from the oxidation of the coal in this way. The difficulties met with arising from the unsatisfactory properties of many of these salts, which are usually obtained in the form of gelatinous, clayey solids, difficult to wash and to obtain in a state of purity suitable for analysis, have led to the abandonment of this reagent.

More promising results have been obtained by acting upon the coal with dilute hydrochloric acid and potassium chlorate. Mr. J. A. Smythe, B.Sc. of the Durham College of Science, Newcastle-upon-Tyne, has undertaken the investigation of this action for the purposes of this Committee.

When finely-divided coal is boiled for several hours with dilute hydrochloric acid, and potassium chlorate added from time to time, the coal gradually assumes a brown colour, and a brown acid collects on the surface of the yellow liquid. The coal, after lengthened treatment, is filtered off, washed, and dried at 100° C. The product

is invariably found to have increased in weight, and when extracted with alcohol or acetone some 30 to 35 per cent of the material is dissolved out by either of these solvents; of the two, acetone is the more powerful solvent, leaving a coal-like insoluble residue. The solution obtained in this manner is next distilled, and after removal of the solvent a dark reddish brown resinous mass is left, which, when finely ground, forms a dark brown homogeneous powder. The finely-divided powder was extracted with benzene; the portion insoluble in benzene was treated with alcohol in which some readily dissolved, leaving a residue sparingly soluble in hot alcohol.

(To be continued).

# SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.[*]

## By GEORGE AUCHY.

(Concluded from p. 249).

### Volhard's Method (continued).

TAUGHT suspicion by the experience thus far had, it was resolved to test every step in the method; and the following determinations were made to see if the temperature of the liquid at the time of neutralisation with zinc oxide had any influence upon the result:—

TABLE VIII.

| Solution heated to boiling with the zinc oxide. | | | Zinc oxide to cold solution. | | |
|---|---|---|---|---|---|
| No. | Manganese taken. | Manganese found. | No. | Manganese taken. | Manganese found. |
| | Per cent. | Per cent. | | Per cent. | Per cent. |
| 1 | 0·40 | 0·49 | 1 | 0·40 | 0·40 |
| 2 | 0·40 | 0·44 | 2 | 0·40 | 0·40 |
| 3 | 0·40 | 0·43 | 3 | 0·40 | 0·40 |
| 4 | 0·40 | 0·47 | 4 | 0·40 | 0·40 |
| 5 | 0·40 | 0·42 | 5 | 0·40 | 0·40 |
| 6 | 0·40 | 0·41 | 6 | 0·40 | 0·39 |
| Solution merely warm. | | | 7 | 0·40 | 0·40 |
| 1 | 1·20 | 1·22 | 8 | 0·40 | 0·41 |
| 2 | 0·80 | 0·83 | 9 | 0·40 | 0·40 |
| | | | 10 | 0·80 | 0·80 |
| | | | 11 | 1·20 | 1·20 |

These results show that neutralisation must be performed in the cold. The writer had always practised this precaution, though for no well-defined reason.

The second series of results in the table also show that there is no tendency to slightly high results, as is the case when titration is done in nitric acid solution (Stone's method).

Volhard, in his article, states that the precipitated manganese dioxide is mixed with protoxide unless some metallic base like zinc oxide, lime, magnesia, &c., be present; and, therefore, in the following experiments on this point it was expected that the results would be poor, since the amount of zinc oxide present was purposely kept as low as possible by making the neutralisation first with sodium carbonate, and then cautiously adding sulphuric acid till slightly acid, the slight excess of acid being then neutralised with zinc oxide.

TABLE IX.

| No. | Taken. | Found. | No. | Taken. | Found. |
|---|---|---|---|---|---|
| | Per cent. | Per cent. | | Per cent. | Per cent. |
| 1 | 0·40 | 0·41 | 4 | 0·40 | 0·41 |
| 2 | 0·40 | 0·42 | 5 | 0·40 | 0·42 |
| 3 | 0·40 | 0·40 | | | |

These results seem to show that this is not a very important source of error. In Särnström's method the point is entirely disregarded.

Five determinations made with 5 c.c. free sulphuric acid (2 to 1) at time of neutralisation with zinc oxide give, instead of the theoretical 0·40 per cent taken, respectively 0·40 per cent, 0·42 per cent, 0·41 per cent, 0·41 per cent, 0·41 per cent.

With 6 c.c. free acid, 0·40 per cent, 0·41 per cent.

With 8 c.c. free acid, the results of Table VIII.

### Särnström's Method.

Messrs. Mixer and Du Bois recommend this method for iron ores (*Journ. Am. Chem. Soc.*, xviii., 385), and give results showing its accuracy. In this method zinc oxide is not used, the neutralisation (hydrochloric acid solution) being effected entirely by sodium carbonate, with care not to add it in greater amount than necessary to precipitate the iron, and the subsequent titration is done without filtering off the ferric oxide thus precipitated. This manner of neutralisation leaves the solution not thoroughly neutralised, and from the foregoing results of this article we should expect high results from Särnström's method. The results given by Messrs. Mixer and Du Bois are, however, excellent results; and this indicates either that neutralisation with sodium carbonate in hot hydrochloric acid solution is not attended with the same phenomena as neutralisation with zinc oxide in nitric and sulphuric solutions, or that in the former process there is a greater tendency of the manganese to precipitate with the iron, and that the error from this source counterbalances the error from titrating in faintly acid and hot solution. But the uniform excellence of the results given by Messrs. Mixer and Du Bois points to the former as the more likely supposition. The method was briefly tested by taking standard manganese solution. Instead of 0·40 per cent manganese taken in one case, 0·44 per cent, and in another 0·38 per cent was obtained. But the test was not a fair one, as there was no iron present to give the exact point of neutralisation as obtained in the regular working of this method. Ferric chloride should have been added, but none was at hand, and the writer postponed further examination of the method for the reason that (as explained by Messrs. Mixer and Du Bois) it is not well adapted to the analysis of steel.

### Colour Method.

The colour method has no kinship to Volhard's, and its consideration is therefore hardly relevant here. But, nevertheless, as it was found necessary in the course of this work to make determinations by this method for comparison with others obtained by Volhard's method in samples almost used up, it might perhaps be just as well to give these colour results in detail, as showing the limits of error in the process when performed by one not an expert in its use.

The results in the table by Volhard's and by Stone's method were obtained by an observance of precautions given—correction of 0·02 per cent in results by the latter method, thorough neutralisation by zinc oxide, &c.

It will be seen that colour method results are quite accurate if a number of colour comparisons be made and the average taken. But if only one test be made the variation may occasionally be 0·02 to 0·03 per cent. But in these determinations the boiling was all done over the naked flame. Closer results can perhaps be had by using the calcium chloride bath for this purpose, as directed in Blair's "Chemical Analysis of Iron."

### Recapitulation.

The sources of error, then, in Volhard's process, as indicated by the foregoing experiments, are :—

1. The incomplete neutralisation by zinc oxide, giving usually high results.

2. The too sudden addition of the necessary excess of zinc oxide, giving frequently low results.

3. The titration in nitric acid solution giving results 0·01 or 0·02 per cent too high.

4. Neutralisation by zinc oxide in hot solution, giving high results.

With regard to the first of these sources of error it may be remarked that Volhard recommends slightly acidifying with nitric acid before titration — to oxidise organic matter. But whatever organic matter may be present capable of being oxidised by nitric acid has already been oxidised, and the organic matter and proto salts present in the sodium carbonate and zinc oxide used for neutralisation is best determined by a blank or dummy test, or better by performing the process with a convenient measured amount of standard permanganate decomposed by hydrochloric acid. Besides the error from titrating in faintly acid solution, a further objection to acidifying with nitric acid is that the manganese dioxide precipitated

### TABLE X.

| No. | First reading. Per cent. | Second reading at a higher dilution. Per cent. | Volhard or gravimetric method. Per cent. | | |
|---|---|---|---|---|---|
| 289 | 0·40 | 0·40 | 0·40 | 0·40 | Volhard. |
| | 0·395 | 0·39 | | | |
| | 0·40 | — | | | |
| 153 | 0·63 | 0·64 | 0·64 | 0·64 | Volhard. |
| | 0·61 | — | | | |
| | 0·639 | 0·65 | | | |
| 503 | 0·552 | 0·547 | 0·56 | 0·56 | Stone. |
| | 0·564 | 0·560 | | | |
| | 0·572 | 0·586 | | | |
| | 0·543 | 0·555 | | | |
| 503 | — | — | 0·423 | 0·41 | Volhard. |
| | 0·426 | 0·416 | | | |
| | 0·42 | 0·425 | | | |
| | 0·42 | 0·42 | | | |
| 505 | 0·495 | 0·49 | 0·49 | 0·49 | Stone. |
| | 0·49 | 0·48 | | | |
| | 0·485 | 0·485 | | | |
| | 0·495 | 0·495 | | | |
| 483 | 0·44 | 0·425 | 0·43 | | |
| | 0·425 | 0·425 | | | |
| 486 | 0·53 | 0·534 | 0·54 | | |
| | 0·54 | 0·546 | | | |
| 471 | 0·38 | 0·37 | 0·38 | 0·38 | Stone. |
| | 0·39 | — | | | |
| 490 | 0·48 | 0·48 | 0·48 | | |
| | 0·48 | 0·486 | | | |
| 493 | 0·438 | 0·445 | 0·46 | 0·46 | Volhard. |
| | 0·47 | 0·466 | | | |
| | 0·468 | 0·47 | | | |
| 507 | 0·43 | — | 0·435 | 0·42 | Stone. |
| | 0·43 | 0·44 | | | |
| 466 | 0·488 | 0·472 | 0·49 | 0·485 | Gravimetric. |
| | 0·497 | 0·498 | | | |
| 481 | 0·49 | 0·475 | 0·469 | 0·455 | Gravimetric. |
| | 0·50 | 0·49 | | | |
| | 0·455 | 0·454 | | | |
| | 0·47 | 0·46 | | | |
| | 0·446 | 0·446 | | | |
| | 0·476 | 0·47 | | | |
| 453 | 0·43 | 0·426 | 0·425 | 0·425 | Stone. |
| | 0·416 | 0·425 | | | |
| 456 | 0·449 | 0·446 | 0·43 | 0·41 | Gravimetric. |
| | 0·427 | — | | | |
| | 0·417 | 0·42 | | | |
| | 0·416 | 0·428 | | | |
| | 0·417 | 0·414 | | | |
| 451 | 0·545 | 0·56 | 0·53 | 0·52 | Gravimetric. |
| | 0·53 | 0·53 | | | |
| | 0·54 | 0·54 | | | |
| | 0·52 | 0·52 | | | |
| | 0·52 | 0·525 | | | |
| | 0·537 | 0·545 | | | |
| | 0·535 | 0·531 | | | |

by titration collects as a film on the glass and obscures the end reaction.

Stone's modification is much easier and quicker than the regular Volhard method; not only because the evaporation to dryness with sulphuric acid is dispensed with, but also, as Mr. Stone points out, because in nitric acid solution the precipitated ferric oxide settles so readily and completely that the filtration from it may be omitted, the clear liquid being decanted from the precipitate. In sulphuric acid solution the precipitated ferric oxide does not settle readily enough for this, and thus considerable time is taken up in making folded filters, and the filter-paper used adds appreciably to the expense of the method.

Mr. Stone performs the neutralisation entirely with commercial zinc oxide, and this is doubtless the reason that his results have always been satisfactory, and he has noticed no necessity for the precaution of thorough neutralisation; for in neutralising altogether with zinc oxide, in the hurry of everyday work one would naturally get a large or a considerable excess of it used, even if not recognising the necessity for such an excess. And as to the precipitation of manganese with the iron, the work in this article would seem to show that to be an exceptional occurrence with nitric acid solution, although of frequent occurrence in sulphuric acid solution if caution be not used in the neutralisation. But as regards neutralisation, the writer considers it more advantageous to use sodium carbonate, or common sal soda first, finishing up with zinc oxide emulsion, for sal soda is much cheaper than commercial zinc oxide. But, as before mentioned, the manganese, organic matter, and proto-salts in these reagents, if any be present, must be allowed for.

Mr. Stone takes 100 c.c. for titration. But 250 c.c. is perhaps preferable on the score of greater accuracy. The writer finds it convenient to use permanganate of strength exactly 0·0056, taking always $3\frac{3}{10}$ grms. of the drillings for analysis. The reading of the scale on the burette then at once gives the percentage of manganese without calculation, except a division by ten.

For the convenience of those unfamiliar with the process details briefly follow, with the precautions found to be necessary in this article printed in italics :—$3\frac{3}{10}$ grms. of drillings. Dissolve in 50 c.c. nitric acid, sp. gr. 1·20. Wash into a 500 c.c. measuring flask. Add about two thirds of the amount of sal soda solution necessary to a complete neutralisation. *If not cold, cool.* Add zinc oxide emulsion till solution stiffens, *avoiding an excess.* Dilute to about three-fourths of the capacity of the flask, mix, and let stand till the ferric oxide begins to settle. See that the solution is colourless. *Add considerable excess of zinc oxide emulsion.* Mix. Dilute to mark. Insert stopper. Mix. Transfer to dry beaker. Mix again. Let settle, and pour off 250 c.c. Titrate in 500 c.c. Erlenmeyer flask (first heating to boiling) with permanganate of strength 0·0056. Make the necessary deduction for impurities in the sal soda and zinc oxide. Divide the number of c.c. permanganate taken by ten. *Deduct 0·02 per cent.*

Following are some comparisons of results by this method with results by Volhard's method, gravimetric method, and colour method :—

TABLE XI.

| No. | Volhard with all precautions. Per cent. | Stone with all precautions. Per cent. | Gravimetric. Per cent. | Colour. Per cent. |
|---|---|---|---|---|
| 1451 | 0·51 | 0·51 | 0·52 | 0·53 |
| 452 | 0·44 | 0·42 | 0·43 | 0·435 |
| 453 | 0·46 | { 0·42 <br> { 0·43 | — | 0·425 |
| 453 | 0·47 | 0·45 | 0·46 | 0·45 |
| 493 | 0·46 | 0·47 | — | 0·46 |
| 466 | 0·41 | 0·41 | 0·41 | 0·43 |
| 466 | 0·49 | 0·49 | 0·485 | 0·49 |
| 481 | 0·45 | 0·46 | 0·455 | 0·469 |
| 153 | 0·64 | 0·65 | — | 0·64 |

# SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

## By W. W. ANDREWS.

(Continued from p. 248).

TIN gives a slightly volatile coating, showing a trace of brown when hot. Potassium thiocyanate, if dropped on the oxide and strongly heated, gives a pale yellowish green, infusible (compare lead). The slight volatility of tin oxide suggests a scale of volatility, of great use in describing the formation of the films on the tablets. The scale runs in the order of increasing volatility,—tin, zinc, cadmium, and mercury. Anything less volatile than tin might be classed as non-volatile.

The iodine solution yields a yellow, reddish brown when hot, the brown fading instantly. Potassium sulphide yields a black with a brown edge, which darkens on heating. Potassium cyanide discharges the colour, which turns black on heating, and when strongly heated shows the pale yellowish green (stannous thiocyanate, $Sn(SCN)_2$; compare lead, bismuth, arsenic, mercury, and zinc). Water decomposes the film with formation of oxy-iodide.

Cobalt nitrate gives the bluish green, which is not so readily attacked by nitric acid as the zinc-green.

Antimony tri- or pentachloride yields with all tin salts a fine purplish blue-black coating, stable in the presence of acids. Potassium thiocyanate decomposes it when heated, and forms the pale green.

These tests with iodine, antimony trichloride, and with potassium thiocyanate, remove tin from the list of metals determinable with difficulty before the blowpipe. They can be depended on through a wide range of mixtures.

Lead yields *per se* a white and yellow; reddish brown when hot. All lead salts fuse into the tablet with the formation of lead plumbate, one of the constituents of glass. Potassium sulphide produces a brownish black, with reddish brown ring.

The iodine solution gives a film which is chrome-yellow, with a band of fainter yellow farther away (oxy-iodide?), and the assay is black. Potassium sulphide yields a spot with the reddish brown edge. Hydrochloric acid destroys the edge at once. Nitric acid wipes the spot off slowly, and sulphuric acid destroys the black and restores the yellow. The very volatile paler yellow on the outer edges is turned to a brighter colour by the same treatment (compare mercury). Potassium cyanide produces a slight paling of the sulphide colour. Potassium thiocyanate on the iodide film gives a black ring, which heated becomes a black spot (compare bismuth). Water wipes off the coating (compare mercury, arsenic, and silver).

The bromide film made by using potassium bromide and potassium hydrogen sulphate presents some interesting differences. It is white with a trace of yellow, the yellow fusing into the tablet. Potassium sulphide gives a spot, greenish for a moment and then black, on which potassium cyanide and potassium thiocyanate have no effect, but is partly destroyed by hydrochloric acid, more rapidly by nitric acid, and completely by sulphuric acid. Potassium thiocyanate, placed on the sulphide and heated, gives a black ring; with greater heat, a yellow; and still greater heat, a greenish grey ring. Potassium cyanide on the iodide film has no effect till heated; then a white. Potassium thiocyanate has no effect on iodide till heated; then a yellowish spot appears (compare tin). The sulphide heated becomes greyish black, on which nitric acid and the other acids have no effect (compare copper).

It is a good illustration of Carnelley's law of colour that in general the bromide film of any metal resembles

the iodide film of an element either in a higher series in its own family, or in the same series in another family toward the left in the natural classification. Thus the bismuth bromide film resembles the iodide film of antimony and lead. Lead bromide resembles tin and thallium iodide. Thallium resembles mercury, and mercury resembles silver in the same way.

Nitrogen with metaphosphoric acid in the nitrates yields an effervescence with the fumes, odour, and reactions of nitrogen tetroxide farther up the tablet, and in the cyanides the odour of hydrocyanic acid. Nitrates with carbonaceous matter yield ammonia, which will cause white fumes to rise from a spot on the tablet moistened with hydrochloric acid. Ross reports that any nitrogen compound with boric oxide yields a tough transparent bead, and, with metaphosphoric acid, purple in the reducing flame with manganese dioxide.

Vanadium gives with metaphosphoric acid a pale yellow in the oxidising flame, and in the reducing flame a green. (Ross).

Phosphorus.—A great desideratum in blowpipe analysis is a good test for this element and the phosphates.

Arsenic yields *per se* a brownish black with a white film falling farther away with odour of garlic and blue flame (compare thallium and tellurium). The iodide coat is white and pale yellow ; the assay wholly volatile. Potassium sulphide, with a drop of hydrochloric acid, forms the yellow sulphide, little affected by acids. If oxalic acid be applied to a sulphide spot, and then hydrochloric acid, no effect is noticeable. The yellow will show up still better next day (compare antimony). If a drop of potassium thiocyanate be placed on the tablet about 1 inch above the assay, and between them a drop of nitric acid and the arsenical vapour be blown over them from the assay, there will generally be formed in the edge of the potassium thiocyanate spot a bright bluish green of unknown composition. All common acids except acetic destroy it. It shows well in the presence of salts of tin and antimony. When it does appear it is decisive for arsenic. This iodide film exhibits a very marked repulsive power for water, probably due to the arsenic oxide which forms with it. Potassium iodide with metaphosphoric acid yields more of the yellow than does the iodine solution.

Antimony *per se* yields a white and yellow band and white fumes. Potassium sulphide yields on this an orange-brown, which is quickly destroyed by a drop of nitric acid.

The iodide film is a fine orange-yellow, far away with yellow nearer the assay, and abundant white fumes. Potassium sulphide yields, especially when heated, an orangered with a rich brown, and then a black beyond the spot. Hydrochloric acid slightly heated destroys it ; nitric acid destroys it instantly, so also does its vapour. Potassium thiocyanate wipes the coating, but heated it yields a fine brown, which is permanent when exposed for months. Potassium cyanide wipes the coat. The orange-yellow sulphide spot, produced on the iodide film obtained with potassium iodide and metaphosphoric acid, is not so susceptible to the action of nitric acid, and is more rapidly destroyed by hydrochloric acid than the one described above.

If arsenic be present with antimony, there will be shown, inside the yellowish orange of the iodide film, a fine peachy pink, which is hard to wet. Stannic chloride yields with antimony, in most combinations, a purplish blue-black, which is remarkably stable (Haanel). It is now being collected in quantity, with a view to the determination of its formula. It will be seen that, with the blue with potassium thiocyanate, the rose-pink, and the reactions of the sulphide with hydrochloric, nitric, and oxalic acids, the presence of arsenic can be easily demonstrated in the presence of antimony, and, as far as experiment has gone, in the presence of any other substances.

Bismuth yields *per se* a yellow ring near the assay, and often a brittle globule. Potassium sulphide gives on the white oxide a brownish black which nitric acid destroys, and on which hydrochloric acid has little effect till heated, when it removes it completely. Sulphuric acid has no effect. Potassium thiocyanate on the oxide produces a yellow ring, and heated a yellow spot turning black. (It is to be noted that potassium thiocyanate itself, when heated or treated with strong acids, shows on the tablet a fine yellow, which further heating renders colourless).

The iodide film is a splendid combination of chocolate-black, crimson, and yellow, the assay turning black. Potassium sulphide forms a chocolate black, soluble in nitric acid and not affected by sulphuric acid. The latter acid on the iodide film produces a black and a dull red edge. This is probably the sulphide formed by the reduction of the acid by the decomposition products of the potassium thiocyanate, which fall with the iodides. It has been noticed, however, to happen with no other metal than bismuth. This reaction is very useful in detecting small quantities of bismuth in the presence of other metals giving dark-coloured films (compare tellurium). Potassium thiocyanate on the iodide wipes it off, forming a yellow ring, but when heated it forms a black spot with a brown ring. Potassium cyanide also wipes the iodide, but when heated forms a dark grey spot. Glacial acetic acid wipes off the yellow and the crimson, but has no effect on the chocolate iodide.

Sulphur.—In looking for a better test for sulphur than the ordinary one with soda and a piece of silver, the stability at high temperatures and the two brilliant and characteristic colours of cadmium sulphide attracted attention, and the fact that it is easily formed in the presence of potassium cyanide. To a solution of cadmium bromide, potassium cyanide was added till precipitation took place, and then the solution of the precipitate as potassium cadmium cyanide. This, dropped on a fragment of the sulphide and heated, will show on the tablet near the assay a brilliant scarlet when hot, and bright yellow when cold. This is not affected by potassium cyanide (compare cadmium oxide). One great advantage of this is, that selenium and tellurium do not yield anything which can be confounded with these colours, selenium giving a greyish brown and tellurium a yellowish brown. Sulphates may be reduced by potassium cyanide, or by glycerol. A sulphide or sulphate fused with potassium cyanide will, if touched with a drop of ferric chloride, show in the tablet the pinkish red of ferric thiocyanate. The sulphur in the tablet causes no trouble.

Selenium and tellurium are further differentiated from sulphur by their characteristic films, which are tests of great delicacy. Twenty-seven varieties of complex sulphides, such as bournonite, tetrahedrite, stannite, &c., and all of the common sulphides and sulphates, were found to respond to this test at once.

Selenium yields *per se* with characteristic odour and flame a fine reddish brown, almost pure red on the outer edges and black on the inner edges near the assay. Potassium cyanide wipes it off, while potassium thiocyanate has no effect, except that if it be heated, a very stable red compound is formed (KSeCN ?).

The iodide film forms in colour very similar to the *per se* coat, but more volatile. Potassium sulphide yields a yellow. Potassium cyanide wipes the iodide film off instantly, and therefore will reveal the presence of any other element not so affected, whose film might be hidden by the pronounced hues of the selenium film. Potassium thiocyanate has no effect, while it and heat wipe off most other coatings, and therefore will reveal the presence of selenium in obscuring associations, such as lead. Sulphuric acid shows a slight tendency to make this coating darker (compare bismuth).

(To be continued)

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**Determination of Acetone in Crude Acetones.**— M. Klor (*Chem. Industrie*) finds the official method used in Germany inaccurate and misleading.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY
SAMPLES OF THE WATER SUPPLIED TO LONDON
FOR THE MONTH ENDING OCTOBER 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
*Water Examiner, Metropolis Water Act, 1871.*

London, November 12th, 1896.

SIR,—We submit herewith, at the request of the
Directors, the results of our analyses of the 189 samples
of water collected by us during the past month, at the
several places and on the several days indicated, from the
mains of the London Water Companies taking their
supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of
samples, one taken daily, from Oct. 1st to Oct. 31st
inclusive. The purity of the water, in respect to organic
matter, has been determined by the Oxygen and Com-
bustion processes; and the results of our analyses by
these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several
samples of water, as determined by the colour-meter
described in a previous report.

In Table III. we have recorded the oxygen required to
oxidise the organic matter in all the samples submitted
to analysis.

Of the 189 samples examined one was recorded as
"clear but dull," the remainder being clear, bright, and
well filtered.

The excessive rainfall of last month has been succeeded
by a nearly average fall in October. The 30 years' mean
is 2·75 inches, and the actual rain has been 2·85, showing
an excess of only 0·10 inch. Our bacteriological results
are shown in the following table :—

| | Colonies per c.c. |
|---|---|
| Thames water, unfiltered .. .. .. .. .. | 2691 |
| Thames water, from the clear water wells of the five Thames-derived supplies.. highest | 67 |
| Ditto　　ditto　　.. .. .. .. lowest | 2 |
| Ditto　　ditto　　.. (12 samples) mean | 19 |
| New River water, unfiltered .. .. .. .. | 671 |
| New River water, from the Company's clear water well .. .. .. .. .. .. .. .. | 4 |
| River Lea water, unfiltered .. .. .. .. | 742 |
| River Lea water from the East London Com-pany's clear water well .. .. .. .. .. | 14 |

Our chemical and bacteriological results have recently
been submitted to severe criticism in a report published
by the London County Council. This is not the place,
neither would time allow us to answer it in detail, but we
cannot neglect the duty of correcting one or two of the
most glaring mistakes.

In order to account for the alleged enormous bacterial
contamination of the London supply, and therefore to con-
demn the efficiency of the treatment of the water by storage
and filtration in opposition to our previous statements and
results, the report declares that we do not conduct the
bacteriological examination in a proper manner. The facts
are exactly the opposite of what the report assumes. It
is the mode of collecting and keeping the samples previous
to the bacteriological examination, adopted by the reporters
to the London County Council, that is unscientific. We
rigidly follow the bacteriological methods of the originator
of the process, viz., Dr. Koch, of Berlin, in the collection
and treatment of the samples and in the plate develop-
ment. Our results have for months been confirmed by
the independent examinations of Dr. Edward Frankland.
To get results entirely at variance with ours the samples
must have been treated in an unscientific way for the
purposes of such investigation. As to the five-hundredth

part of a grain in the gallon of suspended matter in the
London supply, this need cause no scare. No natural or
artificial filtration can avoid causing some amount of sus-
pended matter. No supply from Wales, which must be
subjected to chalk treatment and filtration before it could
be supplied to London, could avoid containing as much,
if not more, suspended matter, so that Londoners would
in such future supply still have to consume 67·5 tons of
peaty mud per annum. Our samples for bacteriological
investigation contain all the suspended matter, and as long
as the results show the relatively small proportion of
microbes that our specimens have done, the public need
not doubt the wholesome quality of the present London
supply, and may safely discard the five hundredth part of
a grain per gallon of innocuous material in the form of
suspended matter. It cannot be disputed that, in spite of
all the allegations of increasing contamination in the
valleys of the Thames and Lea, the water supplied to the
Metropolis has improved during recent years instead of
deteriorating; and with increased storage and effective
filtration we do not doubt the present sources will con-
tinue to furnish a supply adequate in every way to the
needs of the Metropolis.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

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# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, November 5th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. J. B. Knight, S. G. Rosenblum, and J. A. Craw
were formally admitted Fellows of the Society.

The following certificates were read for the first time :—
Henry Edward Aykroyd, Ashwell, Toller Lane, Bradford;
William Ballingall, Ardarrock, Dundee; Charles Bathurst,
Jun., Lydney Park, Gloucestershire; Lauritz Hansen
Bay, The Grammar School, Carlisle; Charles Edward
Browne, 2, Hinton Villas, Cheltenham; George Harold
Cross, B.Sc., Baliol College, Oxford; William Duncan,
Royal Dispensary, West Richmond Street, Edinburgh;
Walter John Elliott, M.A., 5, Dover Place, Clifton,
Bristol; John Thomas Fleet, Rugby, Warwickshire;
George George, Regent Street, Kingswood, near Bristol;
Arthur Croft Hill, Trinity College, Cambridge; Charles
Alexander Hill, Hawthorns, South Road, Clapham Park;
John William Hinchley, Baggeholme Road, Lincoln;
William Trevor Lawrence, B.A., Ph.D., 57, Prince's Gate,
S.W.; Robert Dexter Littlefield, 23, Wightman Road,
Harringay, N.; Thomas Henry Lloyd, Penygraig,
Pontypridd; Thomas William Lockwood, Heckmond-
wike; Edward Seaborn Marks, 111, Cromwell Road, S.W.;
Arthur Stanley Mayfair, Avenue House, Beverley Road,
Hull; William M. Miller, Prye Estate, Wellesley, Penang,
Straits Settlements; Landon Clarence Moore, 19, Meck-
lenburgh Square, W.C; Francis Ambrose Moss, Menzies,
Western Australia; Herbert William Moss, Broken Hill
Proprietary Company, Limited, Port Pirie, South Aus-
tralia; Joseph Terrence de la Mothe, Grand Bacolet
Estate, St. Andrew's Parish, Granada, West Indies;
Alexander Henry Mitchell Muter, The Châtelet, Horley,
Surrey; William Harrison Pearsall, The School House,
Dalton-in-Furness; Henry William Potts, Euroa, Vic-
toria; Frederick Belding Power, 21, Queen Square,
Bloomsbury, W.C.; William Russell, Summerlie, Coat-
bridge, N.B.; Herbert Cecil Seabrooke, The Echoes, Grays,
Essex; William Horace Sodeau, B.Sc., 25, Shore Road,

South Hackney, N.E.; Charles Thompson, Grammar School, Coatham, Redcar; William Henry Walker, Stafford Street, Willenhall, Staffs.; William Watson, M.A., School House, Kingsbridge, South Devon; Edwin Whitfield Wheelwright, B.Sc., Ph.D., The Oaklands, Warley, Oldbury, near Birmingham; John Harrison Wigner, Ph.D., 58, Breakspears Road, St. Johns, S.E.

Of the folllowing papers thoss marked * were read.

*121. "*The Constitution of the so-called Nitrogen Iodide.*" By F. D. CHATTAWAY, M.A.

From the beginning of the present century the black explosive compound formed when a solution of ammonia acts upon iodine, has almost continuously engaged the attention of chemists. No definite conclusion as to its constitution has, however, been arrived at, although from time to time different formulæ have been assigned to it, while, on account of its apparently variable composition, several distinct compounds have been supposed to exist.

The formulæ $NI_3$, $NI$, $NH_2I$, $NHI_2$, and $NH_3NI_3$ have been adopted by various chemists, while others have suggested that a series of different but allied substances exist, derived either from $NH_3$, or a hypothetical substance, $H_3N:NH_3$, by replacement of hydrogen.

A number of experiments made with this substance with a view to the synthesis of hydrazine derivatives having given negative results, an investigation of the compound itself was undertaken.

Nitrogen iodide cannot be obtained dry in a condition suitable for analysis, so that all experiments have to be conducted with an unknown quantity and in presence of water. It is best prepared by adding a solution of iodine in potassium iodide to an excess of a strong solution of ammonia, when it is precipitated as a soft black powder.

Many analyses have shown that its composition does not vary according to the mode of preparation, provided that sufficient care is taken to remove unchanged ammonia, iodine, and the various products of the action. The substance always yields, on decomposition, ammonia and iodine, 1 mol. of ammonia being set free to 2 atoms of iodine. The variations of composition which have been observed are probably due to the substance not having been properly freed from ammonia or iodine, or to a decomposition of greater or less extent having taken place during the treatment of the substance after precipitation. If it be continuously washed with water, all the nitrogen can be removed as ammonium salts, practically pure iodine alone being left. This seems a sufficient explanation of the apparent existence of a series of compounds.

Nitrogen iodide has always been assumed to be a substitution derivative, mainly on the ground that in its preparation a large amount of ammonium iodide is formed.

This, however, is not the sole other product, ammonium hypoiodite also being produced, and, further, more than half the total iodine employed can be obtained in the nitrogen iodide produced. This could not happen if it were a substitution product.

A number of other facts, also, seem to show that it cannot be a substituted ammonia; for example, the invariable production of ammonia, and never of any nitrogen compound containing oxygen in its decomposition by various agents; its formation only from free ammonia, and never from ammonium salts; the fact that iodine does not substitute in $NH_2$ groups, and the production of ammonium iodide when it explodes.

Whenever it is decomposed, ammonia and iodine are always liberated; these may be free or partially combined together, or they may react with the agent effecting the decomposition. An excess of water decomposes the substance, yielding, if light be excluded, ammonium iodide and hypoiodite and free iodine. This action explains the decomposition of the compound by prolonged washing, and the consequent accumulation of iodine in the residue. The ammonium iodide and hypoiodite formed can dissolve a little of the liberated iodine, but a certain amount cannot thus be taken into solution, and consequently remains behind mixed with the undecomposed compound. The percentage of iodine in the residue therefore continually increases, and ultimately only a small quantity of practically pure iodine is left behind.

Potash and soda very easily decompose the substance, liberating ammonia and forming iodide and hypoiodite, or if the solution be heated, iodide and iodate. The oxides of lead and silver suspended in water act similarly, ammonia is evolved, and iodide and iodate of the metal formed.

Finely-divided metals appear to assist the action of the water by combining with the liberated iodine.

Acids, generally speaking, decompose the compound, liberating iodine and ammonia, with the latter of which they combine. The action of hydrochloric acid is peculiar; it seems to form, at first ammonium iodide and iodine chloride.

All substances capable of reacting with iodine at once decompose nitrogen iodide, yielding, in addition to ammonia, the same products that they yield with iodine itself.

Sulphuretted hydrogen forms ammonium iodide and hydriodic acid, while sulphur is precipitated. Sulphurous acid gives hydriodic acid and ammonium sulphate. Sodium thiosulphate liberates ammonia, and forms sodium iodide and sodium tetrathionate. The lower oxides of arsenic and antimony are converted into the higher, with liberation of ammonia and formation of hydriodic acid. Potassium cyanide sets free ammonia, and forms potassium iodide and cyanogen iodide.

On the whole, therefore, it seems that a single substance is formed by the action of ammonia on iodine, and that in this 1 atom of nitrogen is associated with 2 atoms of iodine. Whether the simplest formula that can be given to the substance is $NHI_2$ or $NH_3I_2$ can only be finally settled by a very careful investigation of all its reactions under the most varied conditions; but at present the formula $NH_3I_2$ seems best to accord with the reactions of the substance and express the known facts regarding it.

*122. "*The Carbohydrates of Barley-straw.*" By C. F. CROSS, E. J. BEVAN, and C. SMITH.

This is a continuation of investigations which were the subject of a recent communication (*Trans.*, lxix., 804). The furfuroid carbohydrates isolated by acid hydrolysis from the cereal celluloses afforded evidence of the existence of a hexose-pentose series of tissue-constituents with a definite transition form corresponding with a pentose monoformal. *i.e.*,—

$$C_5H_8O_3 <^O_O> CH_2 = C_6H_{10}O_5.$$

The methods leading to the recognition of this intermediate constitutional form have been applied to the plant taken at various stages of growth during the season 1896. The furfuroids were similarly isolated, and their constitution investigated by (1) osazones, (2) yeast fermentation, (3) the reaction with hydrogen peroxide previously described (*loc. cit.*).

The numbers obtained show a progressive variation. Thus, the osazones are at first of high melting-point (180—190°); the furfuroids are entirely broken down (fermented) by yeast in the neutralised solution, and the peroxide treatment shows negative results, *i.e.*, no evolution of carbon dioxide. From the flowering stage onwards the osazones fall in melting-point; there is increasing resistance of the furfuroids to the action of yeast, and the characteristic reaction with hydrogen peroxide is observed, with increasing proportions of carbon dioxide formed.

These results point to the gradual transformation of a hexose into a pentose derivative.

At the same time the evidence is reviewed upon which these characteristic tissue constituents must be looked upon as having a special constitution or configuration *ab*

*initio,*—*i.e.*, they are assimilated or elaborated in the first instance with the constitutional features which determine their characteristic decompositions, viz., (1) to furfural by the action of condensing acids, (2) to pentose derivatives as a normal incident of their life-history in the plant.

**\*123.** " *The Direct Union of Carbon and Hydrogen.*" By WILLIAM A. BONE and DAVID S. JERDAN.

The authors have continued and extended the experiments of which they gave some account to the Society six months ago (*Proc.*, clxii., 61) and now are in a position to discuss their results more fully.

In their first communication they stated that they had produced methane by passing a slow current of hydrogen, free from hydrocarbon impurities, over purified carbon heated to bright redness in a porcelain tube placed inside a Fletcher injector furnace.

The products of the union of carbon with hydrogen at the temperature of the electric arc have been more thoroughly studied. The electric arc was formed between terminals of purified gas carbon in an atmosphere of dry hydrogen contained in a glass globe standing in a trough over mercury. The arc was maintained in hydrogen for an hour or more, and samples of the gas were drawn off at the end of 5, 15, 30, 45, &c., minutes in each experiment. These were afterwards analysed in a modified form of the McLeod gas-analysis apparatus.

The gases almost always contained small amounts of hydrocyanic acid, due, no doubt, to the presence of a little nitrogen in the hydrogen employed. Acetylene was always present in considerable quantities, and, in addition to this and any other unsaturated hydrocarbon, appreciable quantities of methane were found.

**\*124.** " *The Explosion of Acetylene with less than its own Volume of Oxygen.*" By WILLIAM A. BONE and JOHN C. CAIN.

Continuing their earlier experiments (*Proc.*, cxlii., 170), the authors have exploded mixtures of acetylene with from 29 to 95 per cent of its own volume of oxygen in a leaden coil, some 5 metres long, having an internal diameter of 13 m.m. The coil was closed at each end by a steel tap, and at one end a stout glass firing piece, into which two platinum wires were fused, was fixed between the steel tap and the end of the coil. The other end of the coil was connected with a mercury manometer, so that the pressure change inside the coil after an explosion could be determined.

The coil was immersed in a bucket of cold water, which served to rapidly cool the gases in the coil after an explosion. The coil was filled with the explosion mixture at the ordinary atmospheric pressure by displacement: the mixture was then fired by an electric spark passed across the wires at the firing piece. After the products of the explosion had cooled down to the temperature of the water surrounding the coil, the tap nearest the manometer was opened, and the pressure of the gases inside the coil was read off. In all cases a considerable increase in pressure, varying from 260 to 370 m.m. of mercury, according to the mixture exploded, occurred.

Samples of the products of explosion were collected in each case, and these, together with the original mixtures of acetylene and oxygen, were carefully analysed in a modified form of the McLeod apparatus.

The products of explosion were found to consist chiefly of carbon monoxide and hydrogen, but in addition to these, small, but quite appreciable, amounts of acetylene and carbon dioxide were invariably present.

In their earlier experiments, the authors suspected the presence of a small amount of methane among the products of explosion of certain mixtures of acetylene and oxygen; a more rigid examination of the products has, however, shown that methane is not present in any appreciable quantity.

Further experiments indicate that, although the main resultant reaction may be expressed by such equations as

$$(a) \quad C_2H_2 + O_2 = 2CO + H_2 ;$$
$$(b) \quad 2C_2H_2 + O_2 = 2CO + 2H_2 + 2C ;$$
$$(c) \quad 3C_2H_2 + O_2 = 2CO + 3H_2 + 4C,$$
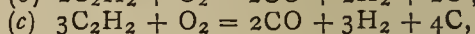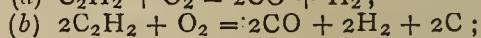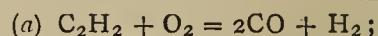
yet some steam is formed; this is evident from the fact that the ratio of the hydrogen to the carbon monoxide in the products is always less than the above equations require. Further, the presence of carbon dioxide in the products would be difficult to explain if no steam were produced.

The small percentages of nitrogen in the products of explosion are due to nitrogen contained in the original mixtures fired.

From these experiments it is evident that, when the electric arc is passed between carbon terminals in an atmosphere of hydrogen, acetylene and methane are both produced. Further, that the rate of formation of these two gases is fairly rapid during the first fifteen minutes of the experiment, after which the rate falls, and finally, after about half an hour, a state of equilibrium between the hydrogen, acetylene, and methane is attained. This equilibrium depends, to some extent, on the voltage employed.

These results led to the inference that methane and acetylene would both be decomposed by the electric arc, and that if the arc is passed long enough a similar state of equilibrium would be arrived at. This conclusion was fully borne out by subsequent experiments, in which pure acetylene or methane was subjected to the action of the electric arc passed between carbon terminals in the same apparatus as that employed in the experiments with hydrogen.

Both methane and acetylene are easily decomposed by the electric arc; during the first ten minutes of the experiment the gas (methane or acetylene, as the case might be) was very rapidly resolved into its elements, large flakes of carbon were formed in the neighbourhood of the terminals, and fell to the surface of the mercury below; the gas in the globe underwent a great increase in volume. much greater than could be accounted for by the mere expansion of the gas by the heat of the arc. A smoky flame rose from the terminals and filled the upper part of the globe. At the end of about ten minutes this extraordinary appearance subsided, after which the arc presented the same appearance as in the case of the hydrogen experiments. After the arc had passed for an hour, the experiment was stopped; samples of the gases were then collected and subsequently analysed.

The principal product in each case was hydrogen with about 9 per cent of acetylene, and small quantities of methane, nitrogen, and hydrocyanic acid. In the experiment with acetylene, a minute quantity of naphthalene was also formed.

**125.** " *The Refraction Constants of Crystalline Salts.*" By WILLIAM JACKSON POPE.

Although a large mass of accurate data concerning the refraction constants and molecular volumes of crystalline substances possessing one, two, or three principal indices of refraction, has been collected, no successful attempt has hitherto been made to deduce a definite general relationship between the refraction constants and the composition of such salts. The author considers that the method used by Tutton, of calculating a single molecular refraction constant for biaxial crystalline substances as the arithmetic mean of the molecular refractions for the two extreme refractive indices, is not a logical one, but that the molecular refraction should be calculated from the mean of all three refractive indices in such cases; the molecular refraction of uniaxial salts should be calculated from a refractive index which is one-third of the sum of the extraordinary index, and twice the ordinary refractive index.

The molecular refraction constants obtained in this way are, within the limits of experimental error, of an additive nature, so that it becomes possible to compile tables of

atomic or equivalent refractions from which the molecular refraction of solid salts may be calculated additively in just the same way as is in general use for liquids.

The molecular refractions of some hundred or so salts have thus been calculated, both from the experimental data and from the table of atomic refractions, and comparison shows a good agreement between both sets of numbers.

The author shows that the molecular refraction of a solid salt, calculated as above described, is not quite the same as that of the salt in aqueous solution. The influence of the solvent is naturally eliminated by dealing with the solid salt alone, and a physical method of deriving valuable information respecting the constitution of solid substances is thus obtained.

126. "*Compounds of Metallic Hydroxides with Iodine.*" By THEODORE RETTIE, B.Sc.

When iodine, dissolved in aqueous potassium iodide, is added to a solution of a magnesium salt, and potash is then carefully added to the mixed solutions, a dark brown precipitate is obtained. The author concludes that this and the somewhat similar precipitates obtained in an analogous manner with solutions of zinc, cadmium, and several other salts, consist of metallic hydrates with a variable quantity of iodine carried down with them, forming compounds resembling lakes.

127. "*Economical Preparation of Hydroxylamine Sulphate.*" By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

Sodium nitrite yields nearly its own weight of hydroxylamine sulphate when carefully sulphonated, by the addition of sodium sulphite, and hydrolysed. In sulphonating, the solution must be kept slightly below $0°$, and the sodium carbonate be closely in proportion to the nitrite of 1 mol. to 2 mols. The hydrolysis in its second stage must not be carried out at a boiling heat, because then much hydroxylamine is destroyed. At $90—95°$ the hydrolysis is satisfactorily effected in two days. After neutralisation, the sodium sulphate is separated, and the hydroxylamine sulphate crystallised out. It is a non-deliquescent salt, soluble in three-fourths of its weight of water at $20°$, and crystallises well.

128. "*The Reduction of Nitrosulphates.*" By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

From a partly quantitative examination of the products of reduction of potassium nitrosulphate by sodium amalgam, it has been ascertained that they include hyponitrite, nitrous oxide, hydrazine, ammonia, nitrogen (probably), sulphite, sulphate, and amidosulphonate. Of 12 mols. of the salt it is estimated that six become amidosulphonate and nitrous oxide, four become sulphite and hyponitrite, and two become sulphate and partly hydrazine, partly nitrogen. The occurrence of hydrazine was discovered by Duden, in 1894; that of sulphate and amidosulphonate is new. The production of sulphate by the sodium is regarded by the authors as another proof that nitrosulphates have not a sulphonic constitution. The formation of amidosulphonic acid is attributed to the salt being a sulphate of a hydrogenisable radicle, and in this respect like no other known sulphate.

129. "*Imidosulphonates.* Part II." By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

Through the kindness of Dr. Raschig the authors have been able to compare the contents of Berglund's Swedish papers on Imidosulphonic Acid and Amidosulphonic Acid, with their own results, which appeared in the *Journal* in 1892 (*Trans.*, lxi., 943). They find that they have succeeded fairly well in making their own work supplementary to his and not a repetition of it. Where there has been overlapping some interesting points are raised.

The normal sodium salt had been prepared by Berglund but only by indirect methods, not by the sulphonation of sodium nitrite. The $\frac{2}{3}$ normal salt he did not prepare.

There is disagreement as to the composition of the oxymercuric salt, and in the present paper new work is submitted, establishing fully, in the authors' judgment, the correctness of their formula, which makes the salt contain the bivalent group $-HgOHgOHg-$, found also in the oxymercuric sulphate, sulphite, and imidosulphonates. What the authors have described as the calcium sodium salt, Berglund mistook for the normal calcium salt. Among the new salts described in this paper are the true normal calcium and the true normal strontium, as well as the $\frac{2}{3}$ normal calcium salt. Berglund also mistook, it appears, the strontium sodium salt for the normal strontium salt. The mercuric sodium salt he duly recognised as such. The mercuric calcium salt has now been prepared, as also a compound of it with mercuric chloride, analogous to apatite, imidosulphonic acid holding the place of phosphoric acid. An oxymercurous salt described is of interest on account of the contrast it shows between imidosulphonic acid and amidosulphonic acid, the latter, like ammonia, resolving mercurous salts into metal and mercuric salts. Lastly, mercurosic salts have been prepared, remarkable in exhibiting a substitution, to varying extent, of the mercurous radicles in the preceding salt by mercuric radicles. The limit of this substitution is expressed in the following formulæ:—

$$O{<}^{Hg_2N(SO_3)_2Hg_2}_{Hg_2N(SO_3)_2Hg_2}; \qquad O{<}^{Hg''N(SO_3)_2Hg_2}_{Hg''N(SO_3)_2Hg_2}$$

Oxymercurous salt.  Oxymercurosic salt.
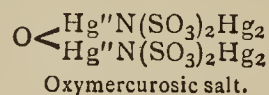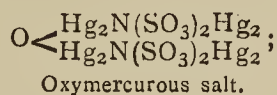
(To be continued).

# CORRESPONDENCE.

## LUCIUM.

*To the Editor of the Chemical News.*

SIR,—In the CHEMICAL NEWS (vol. lxxiv., p. 159) there is an article on Lucium, in which my name is mentioned in confirmation of the properties of lucium as determined by P. Barrière. There must be in this matter a misunderstanding which I should wish to clear up. Certainly, in concert with my son-in-law Dr. E. Hintz, I have concerned myself during the last year almost continually with the chemistry of the rare earths (being induced by the " Glowlight " lawsuits), but I have published no communications which could justify the assumption that a new element like lucium was contained in the thorite which has been submitted to me.—I am, &c.,

Dr. R. FRESENIUS.

Wiesbaden, November 17, 1896.

The Jubilee of Science Teaching in the City of London School.—A strong committee has been secured to promote the " Hall Memorial Fund " in celebration of the jubilee of the introduction of science teaching at the City of London School. This fund is to be available for instituting or founding scholarships for the encouragement of chemistry and experimental science at the City of London School. Among those who have consented to serve on the committee are Dr. W. H. Perkin, Mr. Alexander Mortimer, the Rev. Dr. Abbott, Sir Frederick Abel, Alderman Sir H. E. Knight, Professor Garnett, Mr. A. T. Pollard, Colonel Sewell, Mr. C. J. Wilkinson-Pimbury, Mr. J. Spiller, and Mr. Henry Durham, the last two acting as hon. secretaries. Subscriptions towards the fund will be received and acknowledged by Mr. A. Mortimer, 1, Paper Buildings, Temple, and Mr. J. Spiller, 2, St. Mary's Road, Canonbury.

# CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 18, November 2, 1896.

**New Researches on the Tubercles of Leguminous Plants.**—Ch. Naudin.—The author combats experimentally the theory that leguminous plants derive their supplies of nitrogen from the vital action of bacteria inhabiting the nodosities of their roots. These nodes are most abundant on the roots of the papilionaceous division of the legumens. According to Nobbe and Hillmer the species chiefly if not exclusively concerned is *Bacterium Beyerinckii*. Prof. Schneider, of the University of Minneapolis, says the fixation of nitrogen is effected by six species which he places in the genus *Rhizobium*.

**On Röntgen's Phenomenon.**—Abel Buguet.—It is known that the X rays may be recognised behind a screen exposed to a Crookes tube even if such screen is sufficiently opaque to entirely protect a photographic plate to which it is closely applied. Such an opaque disc of lead exposed between a Crookes tube and a photographic plate rather far from the latter gives a circular spot surrounded by a shaded halo. On arranging such a disc at some centimetres from a tube before a sensitive plate at the distance of 10 or 15 c.c., and carrying the exposure rather far, I have been able, in a series of experiments, to obtain an impression over the entire photographic surface. On arranging upon this plate a series of pins distributed over the surface and all perpendicular to it, I obtained the projections of these pins in white upon grey. All these projections are directed from the centre to the circumference towards the degraded halo already mentioned by several experimentalists. It seems, therefore, impossible to admit that the X rays lean towards the margin of the screen to penetrate behind it, since, if such were the case, the projections of the pins would be directed from the circumference towards the centre of the halo. I cannot admit willingly that the disc of lead may be regarded as transparent in the existing conditions, for blocks of various thickness closely superposed on the disc at various points of the surface on the side of the Crookes tube left no traces on the proof. It seems to be that the peculiar state of space on the free track of the X rays reaches the neighbouring regions which are masked by the screen. The new properties are transmitted with all their characters, those especially which decide the direction of the projection of the pins, characters which fix the direction of the X rays if we aim at comparing the Röntgen radiations with those of light. This transmission of properties is, moreover, an important function of distance, as results from the relative narrowness of the halo. The movement of the molecules of the air, rendered active by radiation, and conveying their new properties behind the opaque screen, does not seem to me capable of explaining the fixity of the phenomenon. In a series of experiments a sheet of lead covered a part of the base of a cylinder of paraffin of 15 c.m. in height resting upon a sensitive plate. It was thus separated from the photographic plate by the paraffin at one end and by an equal layer of air at the other.

**Formation Heat of Lithium Hydride.**—M. Guntz.—Lithium hydride is a very stable substance, differing greatly in its properties from potassium and sodium hydrides.

**Uniformity of the Distribution of Argons.**—Th. Schloesing, jun.—As far at least as living beings are concerned argon may be regarded as very indifferent ; nevertheless its inutility is not really demonstrated. We may conclude with greater certainty than heretofore that argon is, like oxygen and nitrogen, uniformly distributed in the atmosphere, and that it is found normally in the proportion of 1·184 per cent of nitrogen and oxygen.

**Method of the Reproduction of Double Silicates of Potassium and other Bases.**—André Duboin.—We are tempted to approximate glucina to magnesia rather than to alumina on account of the solubility of glucina in potassium fluoride.

**French Essential Oil of Roses.**—J. Dupont and J. Guerlain.—The French oil of roses contains along with terpenic products an ether endowed with a strong lævorotatory power.

**Use of the X Ray for Anatomic Research.**—C. Remy and G. Contremoulins.—Will be inserted in full.

## MEETINGS FOR THE WEEK.

MONDAY, 30th.—Society of Arts, 8. "The Use of Gas for Domestic Purposes" (Cantor Lectures), by Prof. Vivian B. Lewes.

WEDNESDAY, Dec. 2nd.—Society of Arts, 8. "The Teaching of Economics," by W. A. S. Hewins, M.A.

THURSDAY, 3rd.—Chemical, 8. Ballot for Election of Fellows. "Constitution and Colour," by Arthur G. Green. "Some Experiments on Sea-water," by E. Sonstadt. "Derivatives of α-Hydrindone," by C. Revis and F. S. Kipping, Ph.D., D.Sc. "Notes on Nitration," by H. E. Armstrong. "2 : 3'-Bromobetanaphthol," by H. E. Armstrong and W. A. Davis. "Derivatives of Nitrobetanaphthols," by W. A. Davis. "Morphotropic Relations of Betanaphthol Derivatives," by W. A. Davis. "Researches on Tertiary Benzenoid Amines," by Miss C. Evans.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1932.

## PROXIMATE CONSTITUENTS OF COAL.*

(Concluded from p. 262).

THE benzene solution, after removal of the benzene, leaves a dark resinous mass, which, when ground, forms a brown powder, which is dissolved not only by benzene and acetone, but also by ether, chloroform, glacial acetic acid, phenol, and nitrotoluene, but is insoluble in carbon disulphide, petroleum ether, and water. The solutions of this body are all dark brown, almost black, and from these it is always deposited in an amorphous condition. The analysis of this substance gave the following results, from which a formula, $C_{30}H_{22}Cl_8O_{10}$, has been deduced :—

(a) 0·364 grm. gave 0·578 grm. $CO_2$, and 0·086 grm. $H_2O$
   0·293    ,,     0·411  ,, AgCl = 34·67 per cent Cl.
(b) 0·357   ,,     0·571  ,, $CO_2$, and 0·087 grm. $H_2O$.
   0·322   ,,     0·448  ,, AgCl = 34·42 per cent Cl.

|  | a. | b. | Means. | Calculated for $C_{30}H_{22}Cl_8O_{10}$. |
|---|---|---|---|---|
| C .. .. | 43·29 | 43·60 | 43·44 | 43·64 |
| H .. .. | 2·62 | 2·70 | 2·66 | 2·66 |
| Cl .. .. | 34·67 | 34·42 | 34·54 | 34·29 |
| O .. .. | 19·42 | 19·28 | — | 19·41 |
|  | 100·00 | 100·00 | — | 100·00 |

From the alcoholic extraction there was obtained, after removal of the alcohol, a brown solid, very similar in appearance to that obtained from the benzene solution. The results of the analysis of this substance most nearly accord with a formula $C_{24}H_{18}Cl_4O_9$.

(a) 0·420 grm. gave 0·740 grm. $CO_2$ and 0·114 grm. $H_2O$.
   0·463   ,,     0·451  ,, AgCl = 24·05 per cent Cl.
(b) 0·386   ,,     0·680  ,, $CO_2$ and 0·104 grm. $H_2O$.
   0·569   ,,     0·550  ,, AgCl = 23·88 per cent Cl.

|  | a. | b. | Calculated for $C_{24}H_{18}Cl_4O_9$. |
|---|---|---|---|
| C .. .. .. | 48·05 | 48·05 | 48·66 |
| H .. .. .. | 3·01 | 2·99 | 3·04 |
| Cl . .. .. | 24·05 | 23·88 | 23·96 |
| O .. .. .. | 24·89 | 25·08 | 24·34 |
|  |  |  | 100·00 |

From the material left after extraction with benzene and alcohol, which is sparingly soluble in hot alcohol, but soluble in acetone, two substances have been obtained which contain a smaller proportion of chlorine than the above, and from the analytical results appear to have the formulæ $C_{22}H_{14}Cl_3O_5$ and $C_{25}H_{20}Cl_3O_8$. The deep yellow acid filtrate from which the oxidised and unoxidised coal had been removed was shaken out with ether ; the ethereal solution appears to contain some trichloracetic acid. The aqueous solution, after extraction with ether, when concentrated to a small bulk, deposits crystals of potassium chloride, &c., coloured yellow by a colouring matter which is removed by acetone. The acetone solution, on evaporation, gives a reddish viscous liquid, which is dissolved by ether and alcohol, but is insoluble in benzene.
The analysis of the residue left after the evaporation of

acetone showed it to contain some mineral matter, which was left as ash when the substance was burnt. Owing to the small amount at disposal, a further purification was not attempted. The determination of the carbon, hydrogen, and chlorine gave the following :—

(a) 0·4132 grm. gave 0·6460 grm. $CO_2$ and 0·1414 grm. $H_2O$.
   0·4158   ,,     0·2584  ,, AgCl. Cl = 15·36 per cent.
(b) 0·357   ,,     0·5608  ,, $CO_2$ and 0·125 grm. $H_2O$.
   0·4402   ,,     0·2706  ,, AgCl. Cl = 15·20 per cent.
   0·426   ,,     0·015  ,, Ash = 3·52 per cent.

|  | a. | b. |  |
|---|---|---|---|
| C .. | 42·61 per cent | 42·82 per cent |  |
| H .. | 3·80   ,, | 3·88   ,, |  |
| Cl .. | 15·36   ,, | 15·20   ,, |  |
| Ash.. | — | — | 3·52 per cent |

Calculating the percentages of carbon, hydrogen, and chlorine for the substance free from ash, we get amounts corresponding to the formula $C_{33}H_{36}Cl_4O_{20}$, as shown below :—

|  |  | a. | b. | Calculated for $C_{33}H_{36}Cl_4O_{20}$. |
|---|---|---|---|---|
| C | = | 44·18 | 44·39 | 44·29 |
| H | = | 3·94 | 4·03 | 4·02 |
| Cl | = | 15·92 | 15·76 | 15·88 |
| O | = | 35·96 | 35·82 | 35·81 |
|  |  | 100·00 | 100·00 | 100·00 |

Although the action of hydrochloric acid and potassium chlorate on the coal is a slow one, it is much more thorough in its attack than other oxidising agents tried. The coal left after treatment and removal of oxidised product with acetone, when submitted to a second treatment with acid and chlorate of potash, is still further attacked and converted into products similar to those formed in the first instance, and it appears that the proportion of oxidised product increases with each successive oxidation. To study the mode of action, 10 grms. of the coal were boiled with dilute acid and 20 grms. of chlorate of potash, added in small quantities at a time, the action continued for forty-four hours. The dried product was found to have increased by 21 per cent in weight, and of this 62·7 per cent was dissolved by acetone. The residue left after treatment with acetone weighed 5·27 grms., which was again oxidised for forty hours. Of the dried product 74 per cent was removed by acetone, and the remaining 1·26 grms., after a third and similar treatment, gave a product from which acetone dissolved some 77·8 per cent, leaving 0·32 grm. of coal-like insoluble residue.

The analysis of the coal after it had been treated four times with these reagents shows an increased percentage of carbon and hydrogen and the presence of a trace of chlorine.

From the above it is evident that the coal substance is powerfully attacked by hydrochloric acid and potassium chlorate, but the products of this action are for the most part complex substances, from which at present but little information can be derived as to the nature of the materials from which they are formed. These bodies appear to be acidic in properties, and form dark brown solutions with caustic alkalis and ammonia, from which metallic salt solutions, such as barium chloride, lead nitrate, silver nitrate, &c., precipitate out dark coloured gelatinous salts, which are difficult to obtain in a state of sufficient purity for analysis. The attempts to obtain information as to the constitution of these chlorinated compounds have up to the present yielded no satisfactory results.

The composition and physical properties of these chlorinated compounds recall those described by Messrs. Cross and Bevan in their investigations of jute, for example, the substance described by these authors as tetrachlorobastin ($C_{38}H_{36}Cl_8O_{18}$), from which they have obtained protocatechuic acid by fusion with potash.

The treatment of cannel coal with hydrochloric acid and potassium chlorate results in the production of compounds similar to those obtained from the coal of the Hutton seam, the oxidation product soluble in alcohol contained some 24·13 per cent of chlorine.

A sample of bitumen submitted to a similar treatment gave a product from which ether dissolves about two-thirds, the ethereal solution on evaporation leaving a dark viscous residue, which was found to contain 11·06 per cent of chlorine.

Whilst postponing for the present the further study of these chlorinated compounds, Mr. Smythe has begun the investigation of the action of hydrochloric acid and potassium chlorate in "brown coal." For this purpose samples of brown coal were obtained from Brühl, near Cologne; this variety of coal is much more readily attacked than the coal from Durham; it is also noteworthy that while the dry oxidised product from the latter weighs more than the coal, in the case of the brown coal there is a notable decrease in the weight. Further, there is a much larger proportion of the oxidised product soluble in acetone, as the following details of an experiment with 10 grms. of finely ground coal show.

Ten grms. of brown coal boiled for twelve hours with dilute hydrochloric acid and 20 grms. of potassium chlorate; the insoluble mass was filtered off, washed, and dried. The dried solid weighed 6·82 grms.; of this 72·4 per cent was soluble in acetone. The portion insoluble in acetone, viz., 1·88 grms., was treated for twelve hours more with hydrochloric acid and potassium chlorate, giving a solid product of 1·49 grms., of which 79·8 per cent was dissolved by acetone. The chlorinated compounds formed in this manner are very similar in appearance to those obtained from the Hutton seam coal, and probably of a similar character. The crude solid left after the evaporation of the acetone was found to contain some 22·93 per cent of chlorine.

The investigation of these substances, as also the products formed by the oxidation of brown coal with solutions of potassium permanganate, are still in progress.

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# SOME EXTENSIONS OF THE PLASTER OF PARIS METHOD IN BLOWPIPE ANALYSIS.*

By W. W. ANDREWS.

(Concluded from p. 265).

TELLURIUM gives *per se* with flame and odour a brownish black with a white film falling nearer the assay (compare arsenic). Sulphuric acid, if gently heated, shows an effervescent pink of tellurium sulphate. Acetic acid wipes off this coat (compare cadmium). So do the potassium cyanide and ammonia fumes. The iodide film is brownish and purplish black, less brown than the *per se* coat. Potassium cyanide wipes it off in the cold. Potassium thiocyanate has no effect on the purple (compare thallium), and slightly dissolves the brown, and if nitric acid be added a yellow appears. Potassium sulphide darkens the coating a little. Sulphuric acid acts as on *per se* film.

Chromium yields an assay which is dark green when hot and a fine green on cooling. This test can be made very delicate. Metaphosphoric acid gives similar colours.

Molybdenum yields *per se*, and especially by flaming, an ultramarine coating. The oxide film, which forms when the iodine solution is used, comes better by flaming of the film and in presence of vapours of sulphuric acid. A potassium thiocyanate spot, over which the vapours from the assay have swept, exhibits a splendid hyacinthine pink. Metaphosphoric and sulphuric acid vapours aid its formation. It is probably molybdenum thiocyanate $(Mo(SCN)_2)$. If potassium thiocyanate be added to the assay this colour will spread all around the edges of the blue, extending to a distance of two inches from the assay. This very delicate reaction is of special interest, from the fact that it shows that part of the potassium thiocyanate, or at least the radical thiocyanogen, travels undecomposed that distance over the tablet, and that all these films are formed in the presence of moist potassium thiocyanate or thiocyanogen vapours, which will account for the behaviour of some of the films. This pink is decolourised by ammonia, not restored by nitric acid. Sulphuric acid dropped on the tablet will form a blue ring $(MoSO_4)$. Metaphosphoric acid yields blue or bluish green glasses according to the degree of saturation (Ross).

Tungsten and uranium in metaphosphoric in the reducing flame yield, the former a blue and the latter a green glass (Ross).

Fluorine.—If a fluoride be mixed with phosphoric acid and a piece of glass be laid on the tablet about 2 c.m. away from the assay, a fine etched semicircle will show itself after the heating of the assay. The radius of the semicircle is about 3 c.m. long.

Manganese yields with metaphosphoric acid a glass which is violet hot and cold, colourless in the reducing flame, and turning green on the addition of an excess of soda (Chapman, Ross).

Chlorine.—Chlorides, bromides, and iodides of the alkali metals yield *per se* white coatings, which may be distinguished from other white coatings by their flames and by the action of a small quantity of the coating scraped together and mixed with the metaphosphoric acid cobalt glass, which will remain blue on cooling.

A compound of chlorine if mixed with metaphosphoric acid and heated, in the reducing flame (if oxy salt), will cause white fumes to rise from a spot moistened with ammonia situated about 2 c.m. above the assay. If a copper salt be present in the glass or near it, so that copper chloride vapours are formed, and these are allowed to sweep over a spot of nitric acid and then over one of potassium thiocyanate, near the assay a yellowish brown coating of cupric chloride will form with an azure blue flame, and beyond the potassium thiocyanate spot a fine blue-black, very volatile (see copper).

A bromide with potassium cyanide added to it and the fused mass laid upon a copper glass and a drop of nitric acid added, a fine red will show itself. Bromides with metaphosphoric acid saturated with copper, upon blowing, yield a fine and very volatile reddish violet coating. If a bismuth salt be exposed to the hot vapours, it will yield a yellow coating. The spot on the tablet moistened with starch paste, not too near the assay, will turn yellow.

Similarly treated iodine compounds yield violet vapours, a violet in the glass appearing with effervescence, and with copper salt they yield a white coating, with bismuth scarlet and chocolate, and with starch a bluish black.

Iron gives an iodide film too delicate in colour to show up well, either on the white or the black surface. Its presence can be shown by a red colouration after blowing hydrochloric acid vapours over the tablet, to turn all ferrous compounds into ferric, and then adding a drop of potassium thiocyanate to the coating. It is difficult to obtain plaster of Paris sufficiently pure not to give this reaction for iron. Such reaction can, however, be readily distinguished from that given by an assay. Metaphosphoric acid gives a luminous yellow when hot, which is perfectly colourless when cold. A drop of acid on this to produce ferric compounds, followed by a drop of potassium thiocyanate, will show the red of ferric thiocyanate, which is decolourised by phosphoric acid, but not by hydrochloric acid. Made in this way, this test is not too delicate to show the iron of composition. An assay of iron treated with a drop of sulphuric acid and heated will show on the tablet a film of Venetian red.

Cobalt yields a glass blue hot, and violet cold; permanently blue if alkali be present. Boron trioxide acts similarly. With the iodine solution a spot around the assay turns pink, then deep blue on heating, and then black.

Nickel with boron trioxide separates as green fragments, which may be gathered by solution of the glass in water, and then the separated nickel (as any nickel compound) will yield in metaphosphoric acid, a reddish brown when hot and amber yellow when cold (Ross).

Palladium gives a dull blue-black film with the iodine solution, which is very characteristic. The assay turns dull black.

Osmium yields *per se* a greenish black. The iodide film is a combination of olive green, dove, and slate colours, with red appearing around the lower edges. The edge of the coating nearest the assay shows greenish brown, and the assay itself will be closely surrounded with an iridescent black film. Potassium sulphide turns the coating somewhat darker, which, heated, becomes a brownish film, which is wiped off by hydrochloric and nitric acids, and not affected by sulphuric acid and potassium cyanide. On the iodide films sulphuric acid has no effect; potassium thiocyanate has none till heated, and then it turns brown. Hydrochloric and nitric acids

remove the film. Potassium thiocyanate dropped on the tablet over an inch from the assay before the coating is deposited, will, when the vapours sweep over it, turn to a fine brick red, destroyed by potassium cyanide and the acids.

Potassium bromide and potassium hydrogen sulphate give a pinkish brown (compare copper). Potassium sulphide produces a grey not affected, which turns darker on being heated, destroyed by acids, and not affected by potassium cyanide.

Iridium yields with the iodide solution an indistinct brownish yellow coating and a potassium thiocyanate spot, which in tint resembles the molybdenum spot, but it is covered with dots of darker pink.

Platinum gives an infusible grey film. Ruthenium and rhodium are being investigated.

All these reactions have been obtained from a large number of the compounds of each element except in the cases of osmium, indium, and iridium. The writer will be glad to hear of any cases in which they fail, and to receive specimens of combinations which cannot be unlocked by this method. One grm. weight of any alloy is sufficient. The next work to be undertaken is to exhaustively determine the lowest percentage of any metal which can be determined with certainty in the presence of one, two, or any number of other metals, to describe the characteristic effect that one metal has on the coating yielded by another when they are deposited together, and to determine the value of each metal as an interfering element.

### Covered Tablets.

The tablets are easily cut with a knife, and therefore they can be used in various ways. Open tube work can be performed on a tablet if a groove be cut lengthwise of a tablet and laid upon another, groove down. A small pit for the assay is cut in the lower one about one centimetre from the end. The groove is cut so that its narrowest part is just above the assay pit, and from that point to the lower end it flares into a half funnel form, and into this the flame is blown. By regulating the size of the groove at its narrowest part the amount of air which will flow over the assay may be regulated. This method is of great use when very small quantities of precipitates are to be tested. For instance, five-tenths m.grm. of arsenious oxide gave in one experiment a narrow coating one-half inch long on each tablet. This gives ample opportunity for making confirmatory tests. Various reagents may be placed along the groove to be acted on by the vapours, gold leaf for mercury, potassium cadmium cyanide and lead acetate for hydrogen sulphide fumes, starch, bismuth, and antimony solutions for iodine, copper sulphate for chlorine, &c.

If a coating be made, or a small piece of volatile salt be placed in a small pit in the tablet and a thin tablet be placed over it, it is found that if potassium sulphide, or potassium thiocyanate be dropped on the upper tablet, and the flame be directed upon the drop, they will pass through the tablet, and reactions will take place away from the air. After a few seconds blowing the upper tablet will be found to be floating on a layer of hot gas, which flows between the two smooth surfaces. Tin and arsenic, and other substances easily oxidising in the air, form their sulphides very readily under these conditions. Potassium thiocyanate forms sulphides. It is in this way possible, by using ammonium hydroxide or hydrochloric acid, to form the sulphides in the presence of moist acid or alkaline vapours.

Other methods of using the tablets will be described later.

In teaching research methods, the plaster of Paris method is one of the finest instruments to use with beginners. In the course of an hour a student will have been able to make from twenty to forty different tests, and without any delay in preparing solutions, or in waiting for filtration to take place, he will have produced

the oxide, sulphide, chloride, bromide, and iodide of a given metal, and will have noted their colours, manner of deposition, volatility, solubility in several reagents, and the behaviour of the assay itself at high temperatures, and will have ransacked his vocabulary to find terms to describe the phenomena in his written notes. His skill in manipulation and his powers of observation are kept in liveliest exercise, and his independence developed, for it is quite possible to give each student in a large class his own problem. In no other laboratory work do the compelled acts of judgment follow each other as rapidly. There are many problems which may be set requiring reference to standard chemical literature, and many simple, and some very difficult equations of reactions to be written.

Not the least valuable consideration from an educational standpoint is the æsthetic quality of the work. All the coatings are symmetrical in form and beautiful in shading, and many of them in brilliancy of hue and in delicacy of shading rival the most splendid colours of flowers. This gives added interest to the work, and is of great value since adult students are so frequently found to be greatly deficient in the colour-sense, as children are not. There has not been opportunity to compare the shades of these films with the descriptions given in the "Standard Dictionary." When this has been done exact training can be given in colour laaguage also.

Apology is offered for publishing the results of this research at this stage, when so many unsolved problems stand along its path, but this much is given in order that the practical value of these reactions and methods may be put to the test.

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# THE CHEMISTRY OF THE CONSTITUENTS OF MONASITE.

By PAUL DROSSBACH.

As it is known the chief constituents of the monasite form a by-product of the manufacture of thorium nitrate. They serve for the production of easily fusible glasses capable of resisting fluctuations of temperature, whilst didymium is used for decolourising glass.

The monasites of commerce form three varieties without reference to that from Norway—(1) Brazilian monasite, fine polished grains of an amber-yellow ; (2) Carolina monasites from Cleveland county, well-developed sharply angular yellow crystals mixed with the integrating constituents of the local laterite from which monasite has been formed (chrome-iron, titanite, garnet, and zircons) ; (3) Monasite of the north-eastern spurs of the Blue Mountains, dark-brown crystals from the size of a hemp seed to that of a pea. The last-mentioned variety is the material of the present work.

There were used each time 3000 to 4000 kilos. of the mineral carefully prepared and very finely ground. The mean composition of the mineral was as follows :— $Ce_2O_3 = 21\cdot4$ per cent ; $La_2O_3 = 14$ per cent ; $Di_2O_3 = 28\cdot8$ per cent; oxides of the erbium group $= 1\cdot5$ per cent ; thorium oxide, $ThO_2 = 8\cdot0$ per cent ; alien oxides of the cerium group about $\frac{1}{2}$ per cent. The residue consisted of phosphoric acid, silica, and the mechanical impurities of monasite. The specific gravity of the mineral was constant at $5\cdot13$. The geological details of the monasite deposits will be considered elsewhere.

*Methods of Separation.* — The monasite, very finely ground, was opened up in the well-known manner, and after the feebly-basic thorium has been fractionated out, the lye obtained by lixiviation with cold water is at once mixed with a large excess of concentrated sulphuric acid. On the application of heat the sulphates of cerium, didymium, and lanthanum (very sparingly soluble in dilute sulphuric acid) separate out, whilst the sulphates

of the true erbium group remain in solution. A saturated solution of sodium sulphate is formed by partial neutralisation with soda. In this liquid the sulphates of the cerium elements are perfectly insoluble, and separate out in the state of double salts.

The sulphuric solution of the erbium elements is now advantageously precipitated with oxalic acid in order to eliminate iron and phosphoric acid. The elaboration of the oxalic precipitate will be described below.

*Separation of Cerium from Lanthanum and Didymium.* —The procedure depends on the fact that cerium sesquioxide as a hydrate or in a solution kept constantly neutral is oxidised by permanganate according to the equation—

$$3Ce_2O_3 + 2KMnO_4 + H_2O = 6CeO_2 + 2KOH + 2MnO_2.$$

The procedure takes practically the form that the mixture of oxides is precipitated with ammonia in an aliquot part of the liquid, and the cerium is titrated with permanganate. We then add to the main quantity a small excess of permanganate and the calculated quantity of alkali, when the cerium falls down quantitatively but accompanied with a didymium constituent.

The main quantity of the didymium can be extracted by a little dilute nitric acid, and then the cerium with stronger acid, leaving a residue of manganese dioxide. The cerium dioxide solution is mixed, according to Auer, with ammonium nitrate, and the double salt which is easily crystalline is obtained by evaporation.

*Separation of Lanthanum and Didymium.*—The fractionation with ammonia formerly proposed was not successful, since both lanthanum and didymium oxide expel ammonia from its salts. It is superseded by Auer's oxide process. Equally good results are obtained more simply by fractionating the nitrate solutions with soda lye. Soda lye is added to the general solution until the supernatant liquid is free from any absorption-spectrum. The solution then contains the bulk of the lanthanum free from didymium ; the precipitated hydrate in turn on digestion with crude didymium lye gives up gradually all its lanthanum to the latter liquid. The lanthaniferous didymium lye is added to a subsequent portion.

*Scission of Didymium.*—I have not tried the method followed by Auer and Schottländer, and refer solely to that fraction of didymium which is deposited along with the cerium.

The original monasite-didymium displays a great number of absorption bands ; one between A and B, a narrow stripe between B and C, a similar one to the left of D, a broad band to the right of D, a narrow stripe to the left of E, a stripe at E to the left of B, three delicate stripes and a broad band between F and G.

The didymium ingredient precipitated along with cerium shows merely the narrow stripe to the left of D, as also two strong sharp bands to the right of D. Details are reserved for a future investigation.

*Separation of the Erbium Elements.*—The above mentioned oxalic precipitate, free from didymium, is converted into hydrate by treatment with potassa lye (not soda lye), dissolved in nitric acid, and the nitric solution precipitated with magnesia ; the filtrate contains all the yttrium if the precipitation is repeated twice, and the precipitate all the ytterbium, erbium, and probably a new oxide. If the mixture of oxides is fractionated either according to Auer's original method or according to the basic nitrate procedure mentioned under lanthanum, almost all the ytterbium is collected in the first fractions, since ytterbium in this process, according to Auer, is precipitated before erbium. All these first fractions as far as they show no trace of absorption are collected together. That we have here to do with ytterbium can in first place be judged only from the atomic weight. The statements published on ytterbium do not permit us to decide. But as the periodic system assumes two oxides whose atomic weights fall very near that of ytterbium, it is in consequence of the want of sharp reactions very possible here a new oxide may be present.

The finely coloured erbiferous liquid is now so long precipitated with soda lye (much diluted and added very gradually until the supernatant liquid no longer shows any trace of an absorption spectrum). The erbium hydroxide is dissolved in sulphuric acid, and the pure sulphate is obtained in splendid rose-coloured crystalline crusts. The mother-liquor contains considerable quantities of the oxide described below.

The solution freed from erbium may be conveniently again precipitated with oxalic acid in order to remove impurities which have accumulated or which have been derived from the reagents.

The oxalates may be converted into oxides or hydrates by ignition or by treatment with potassa lye. It is advisable to precipitate fractionally the above sulphatic mother liquor (poor in erbium), and again to precipitate with oxalic acid the filtrate when freed from erbium. The hydrate thus obtained is again converted into a nitrate, and as its concentrated solution often still shows traces of an erbium spectrum. this is eliminated in the manner mentioned. If the elimination of the didymium has not been previously effected with care, didymium lines are still displayed. Didymium is, however, so strongly basic that in the following operations it always adheres to the last portions. The nitrate solution thus obtained free from erbium was submitted in two portions, A to six-times fractionation with soda-lye, B to five times repeated fractional crystallisation of the sulphates by admixture with sulphuric acid and concentration.

The mean atomic weight of the elements perfectly free from erbium as calculated from the sulphates is 114 if the oxide is $R_2O_3$. In the fractionated precipitation of the nitrates the first fraction still showed erbium and had the atomic weight 157; the second, third, fourth, and fifth had respectively the atomic weights 100·5, 98·5, 98·5, 100·5; the sixth fraction was 109·7. The last still retained didymium and lanthanum, as the further treatment showed. The two intermediate sulphate fractions yielded a similar result, whilst the terminal members showed higher atomic weights (Er, Di).

The four intermediate fractions showed in accordance, along with the reactions of the group, the following behaviour :—The sulphate is relatively easily soluble in water, and only concentrated solutions yield crystalline crusts when heated. The solutions yield no absorption-spectrum. The oxalate is soluble in solutions of the alkaline oxalates. Hydrogen peroxide and ammonia throw down a white precipitate (peroxide?). The carbonate, like the hydrate, is readily soluble in an excess of alkaline carbonate.

Only the solution of ammonium carbonate gradually deposits carbonate, but not on the addition of ammonia. The oxalate is soluble in carbonates. It is distinguished from thorium by its strong basicity and by the solubility of the double sulphates of the alkaline metals.

As an element of the above named properties and of an atomic weight close upon 100 finds no place in the atomic system, further investigations must determine whether a different valence than that assumed belongs to the above-named constituent of monasite, or if we have to do with a unitary substance. This investigation the author reserves to himself.—*Berichte*, xxix., No. 15, p. 2452.

## COLOUR PHOTOGRAPHY.*

By Professor G. LIPPMANN, Membre de l'Institut (France),

THE problem of colour photography is as old as photography itself. The desire of fixing the colours as well as the design of the beautiful image thrown on the screen of the camera, very naturally occurred to the earliest observers. Since the beginning of this century three distinct solutions of the problem have been realised.

The first solution, not quite a complete one, is founded on the peculiar properties of a silver compound, the violet subchloride of silver. E. Becquerel (1860) converted the surface of a daguerreotype plate into this silver compound, and by projecting on it the image of the solar spectrum, and other objects, obtained good coloured impressions. Poiteven substituted paper for the silver plate as a substratum. No other substance has been discovered that can play the part of the subchloride of silver. Moreover, the image is not fixed, in the photographic sense of the word ; that is, the coloured impression is retained for any length of time in the dark, but it is blotted out by the action of daylight. The reason of it is this : the Becquerel images are formed by coloured silver compounds, which remain sensible to light ; so that they are destroyed by the continued action of light, in virtue of the same action which gave them birth. Despite the numerous experiments made by Becquerel, Poiteven, Zenker, and others, no substance has been found that is capable of destroying the sensibility of the subchloride for light without at the same time destroying its colour.

The second method for colour photography is an indirect one, and may be called the three-colour method. It was invented in France by Ch. Cros, and at the same time by M. Ducos du Hauron (1869). German authorities claim the priority of the idea for Baron Bonstetten. Three separate negatives (colourless) are taken of an object through three coloured screens. From these three positives (equally colourless) are made ; and, lastly, the colour is supplied to these positives by means of aniline dyes or coloured inks. Thus three-coloured monochromatic positives are obtained, which by superposition give a coloured image of the model. In the ingenious process lately invented by Prof. Joly, the three negatives, and apparently the corresponding three positives, are obtained interwoven on one and the same plate. The three-coloured method can give a very good approximation to the truth, and has probably a great future before it. We may call it, nevertheless, an indirect method, since the colours are not generated by the action of light, but are later supplied by the application of aniline dyes or other pigments. Moreover, the choice of these pigments, as well as of the coloured screens through which the negatives have been obtained, is in some degree an arbitrary choice.

The third and latest method by which colour photography has been realised is the interferential method, which I published in 1891, and the results of which I beg to lay before you. It gives fixed images, the colours of which are due to the direct action of the luminous rays.

For obtaining coloured photographs by this method, only two conditions are to be fulfilled. We want (1) a transparent grainless photographic film of any kind, capable of giving a colourless fixed image by the usual means ; and (2) we want a metallic mirror, placed in immediate contact with the film during the time of exposition.

A mirror is easily formed by means of mercury. The photographic plate being first enclosed in a camera slide, a quantity of mercury is allowed to flow in behind the plate from this small reservoir, which is connected with the slide by a piece of india-rubber tubing. The slide is then adapted to the camera, and the action of light allowed to take place. After exposure the slide is separated from the camera, the mercury reservoir lowered so as to allow the mercury to flow back into it ; the photographic plate is then taken out, developed and fixed. When dry, and examined by reflected light, it appears brilliantly coloured.*

The sensitive film may be made either of chloride, iodide, or bromide of silver, contained in a substratum

* The glass of the photographic plate has to be turned towards the objective, the film in contact with the metallic mirror.

either of albumen, collodion, or gelatine. The corresponding developers, either acid or alkaline, have to be applied; the fixation may be cyanide or bromide of potassium. All these processes I have tried with success. For instance, the photograph of the electric spectrum now projected before your eyes, has been made on a layer of gelatino-bromide of silver, developed with amidol, and fixed with cyanide of potassium.

As you see, bright colour photographs may be obtained without changing the technique of ordinary photography: the same films, developers, and fixators have to be employed; even the secondary operations of intensification and of isochromatisation are made use of with full success. The presence of the mirror behind the film during exposure makes the whole difference. From a chemical point of view nothing is changed, the result being a deposit of reduced silver left in the film, a brownish, colourless deposit. And yet the presence of a mirror during exposure causes the colourless deposit to show bright colours. Of course we want to know how this is done; we require to understand the theory of those colours.

We all know that colourless soap-water gives brilliant soap-bubbles; the iridescence of mother-o'-pearl takes birth in colourless carbonate of lime; the gorgeous hue of tropical birds are simply reflected from the brownish substance which forms the feathers. Newton discovered the theory of these phenomena, and subjected them to measurement; he invented for the purpose the experiment called by the name of Newton's rings. Newton showed, as you know, that when two parallel reflecting surfaces are separated by a very short interval, and illumined by white light, they reflect only one of the coloured rays which are the constituents of white light. If, for instance, the interval between the reflecting surfaces is only 2/10,000 of a millimetre, violet rays are alone reflected, the rest being destroyed by interference: that is, the two surfaces send back two reflected rays whose vibrations interfere with one another, so as to destroy every vibration except that which constitutes violet light. If the interval between the reflecting surfaces be augmented to 3/10,000 millimetre, the destruction of vibration takes place for every vibration except that of red light, which alone remains visible in this case.

If we consider now this photograph of the spectrum, and especially the violet end of the image, we find that this is formed by a deposit of brown reduced silver. In the case of an ordinary photograph, this deposit would simply be a formless cloud of metallic particles; here the cloud has a definite stratified form; it is divided into a number of thin equidistant strata, parallel to the surface of the plate, and 2/10,000 m.m. apart. These act as the reflecting surfaces considered by Newton, and as they are at the proper distances for reflecting violet rays, and these alone, they do reflect violet rays.

The red extremity of the photograph is equally built up of strata which act in a like manner; only their distance intervals here amount to 3/10,000 m.m., and that in the proper interval for reflecting red light. The intermediate parts of the spectral image are built up with intermediate values of the interval, and reflect the intermediate parts of the spectrum.

The appearance of colour is therefore due to the regular structure above described, imprinted on the photographic deposit. The next question is—How has this very fine, peculiar, and adequate structure been produced?

It is well known that a ray of light may be considered as a regular train of waves propagated through the ether, in the same way as waves on the surface of water. The distance between two following waves is constant, and termed the wave-length; each sort of radiation, each colour of the spectrum, being characterised by a particular value of the wave-length. Now when a ray of light falls on a sensitive film, this train of waves simply rushes through the film with a velocity of 300,000 kilometres per second; it impresses the film more or less strongly, but leaves no record of its wave-length, of its particular nature or colour, every trace of its passage being swept out of form by reason of its swift displacement. The impression therefore remains both uniform and colourless. Things change, however, as soon as we pour in mercury behind the plates, or otherwise provide for a mirror being in contact with it. The presence of the *mirror* changes the propagated waves into *standing* waves. The reflected ray is, namely, thrown back on the incident ray, and interferes with its motion, both rays having equal and opposite velocities of propagation. The result is a set of standing waves—that is, of waves surging up and down, each in a fixed plane. Each wave impresses the sensitive film where it stands, thus producing one of these photographic strata above alluded to. The impression is latent, but comes out by photographic development. Of course the distance between two successive strata is the distance between two neighbouring waves; this, theory shows, is exactly half the wave-length of the impressing light. In the case of violet, for instance, the wave-length being 4/10,000 m.m., half the wave-length in the above quoted distance of 2/10,000 m.m.; this, therefore, is at the same time the interval between two successive standing waves, in the case of violet light the interval between two successive photographic strata, and at last it is the interval required to exist, according to Newton's theory, for the said strata reflecting violet rays, and making these alone apparent when illuminated by white light.

The colours reflected by the film have the same nature and origin as those reflected by soap-bubbles or Newton's rings; they owe their intensity to the great number of reflecting strata. Suppose, for instance, the photographic film to have the thickness of a sheet of paper (one-tenth of a m.m.), the fabric built in it by and for a violet ray is five hundred stories high, the total height making up one-tenth of a m.m. Lord Rayleigh, in 1887, has proved *à priori* that such a system is specially adapted to reflect the corresponding wave of light.

(To be continued).

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**Detection of the Benzoyl Radicle in Organic Substances.**—E. Léger (*Bull. Soc. Chim. de Paris*).—The characteristic is an odour of peppermint, or, in other words, of benzoic ethyl ester.

**Detection of Tartaric Acid by means of Resorcin.**—G. Denigés. — Mohler's solution of resorcin prepared with concentrated sulphuric acid is not very permanent. To avoid this defect Denigés dissolves 2 grms. white resorcin in 100 c.c. water, and adds ½ c.c. coecentrated sulphuric acid. This solution is quite permanent. If oxidising agents are present, they are first reduced with zinc and sulphuric acid.—*Zeit. Anal. Chem.*

**A Reagent for Sugar.**—A. Conrad (*Apoth. Zeitung*).—Cane-sugar, grape-sugar, and levulose in solutions containing 0'1 per cent, if boiled for three minutes with 0'1 resorcin and 1 c.c. hydrochloric acid, yield a colour rose to carmine. To detect milk-sugar in cane-sugar the author boils 1 grm. milk-sugar in 10 c.c. water, adds 0'1 grm. resorcin, 1 c.c. hydrochloric acid, and boils for five minutes. In the absence of cane-sugar the solution does not turn red.

**Recognition of Mineral Acids in presence of Acetic Acid.**—G. Griggi.—(*Chemiker Zeitung*). The author spreads on a flat porcelain capsule 1 c.c. of the liquid in question, especially vinegar. He then adds one drop of an alcoholic solution of magenta, containing 25 grms. magenta dissolved in 100 c.c. of alcohol at 90 per cent by volume. On mixing both liquids, if any acetic acid is present, the colour of the magenta remains unaltered, but if a mineral acid is present, the liquid takes a dirty yellow colour. On neutralising with an acid the original colour of the magenta is restored.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.
*Ordinary Meeting, November 5th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Continued from p. 269).

**130.** "*Amidosulphonic Acid.*" By E. DIVERS, M.D., F.R.S., and T. HAGA, D.Sc.

Except in the field of organic chemistry, nearly all that is known of amidosulphonic acid and its salts we owe to its discoverer, Berglund. Outside his work, in 1876, there is only to be mentioned that Fock has described its crystals and Raschig discovered a simple and excellent, though costly, method of preparing it by sulphonating hydroxylamine.

Of the additions now made by the authors to the knowledge of this acid, the following are the most prominent. Amidosulphonic acid is largely precipitated from its solutions by sulphuric acid. This fact makes the preparation of the acid from sodium nitrite very easy. Its preparation from this source is also very inexpensive; for when the nitrite has been sulphonated, and the product hydrolysed, the solution neutralised, and sodium sulphate crystallised out, there only remains to add some concentrated sulphuric acid, in order to get amidosulphonic acid almost pure, and in quantity equal in weight to at least three-fourths of the nitrite worked upon.

Amidosulphonic acid combines with mercuric oxide only to form a basic insoluble compound. The acid precipitates the same compound from a solution of mercuric nitrate, which it can completely decompose, its mercury compound being insoluble in dilute nitric acid. More remarkable is the fact that this compound is soluble in alkalis. In its degree of basicity it agrees with the oxy-mercuric sulphate, sulphite, and imidosulphonates, and may therefore be formulated as—

$$(H_2NSO_3HgO)_2Hg,2H_2O.$$
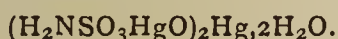
But, since potassium hydroxide dissolves it without decomposing it, and that, regarding its amidosulphonic acid as an amine, it behaves exactly like a mercurammonium compound with Pesci's reagent (ammonium bromide), it may be taken to be—in alkaline solution at least—a sulphonated mercurammonium hydroxide,—

$$Hg_3N_2(SO_3K)_2(OH)_2,2H_2O.$$
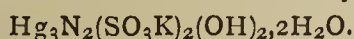
Amidosulphonic acid shows, again, a likeness to ammonia in serving to prevent precipitation of silver nitrate by potassium hydroxide. When the amidosulphonate is not in excess, a bright, ochre-yellow, colloidal substance can be precipitated from solutions of moderate dilution. Much water decomposes it, and forms with it a colloidal brown solution (apparently of silver oxide). Its composition seems to be expressed by the formula $AgHNSO_3K$. Double decomposition between silver nitrate and potassium amidosulphonate does not take place when their solutions are mixed. The normal silver salt is well known.

The first action of heat upon amidosulphonic acid is very interesting. It melts at 205°, but not without decomposing, to a liquid which solidifies to a transparent vitreous mass, on cooling. The properties of this mass, which is formed without gain or loss in weight to the acid, show it to be composed of ammonium pyrosulphate and ammonium pyro-imidosulphonate in molecular proportions, along with 7 to 10 per cent of unchanged acid. This transformation of the acid by heat is a striking example of intra-molecular decomposition and of cumulative re-solution in the direction of ammonia and water for hydration and salt formation. The behaviour of the mixed pyro-salts, when further heated, is described in the author's paper, but must be passed over here. Anhydrous salts of amidosulphonic acid are largely converted by heat into imidosulphonates and ammonia, but also into sulphates and gases. The decomposition of the barium salt, for instance, is nearly represented by the equation—

$$3Ba(SO_3NH_2)_2 = 3BaSO_4 + HN(SO_3NH_4)_2 + \; + NH_3 + NS + N;$$
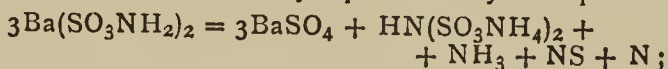
but it is only this salt that yields nitrogen sulphide.

**131.** "*Molecular Conductivity of Amidosulphonic Acid.*" By J. SAKURAI.

The molecular conductivity of amidosulphonic acid was determined by means of a Kohlrausch's universal bridge; the result shows that it is a strong monobasic acid, being nearly comparable with iodic acid. The author compares, at different dilutions, the degree of dissociation of amidosulphonic acid,—

$$O_2S{<}^{NH_2}_{OH},$$
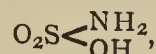
with that of sulphurous acid,—

$$O_2S{<}^{H}_{O H},$$
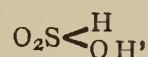
at the same dilutions, and shows that the former acid is much stronger than the latter. This result, he points out, is interesting from the fact that the influence of the $NH_2$ group upon the strength of organic acids generally is just of the opposite character, as is well known, and gives a confirmation of the view already published (*Proc.*, 1894, cxxxvii.) on the constitution of glycocin and other organic amido-acids. The fact that organic amido-acids are weaker than the non-amidated acids, whilst amidosulphonic acid is stronger than sulphurous acid, of which it is the amido-derivative, shows that mere presence of $NH_2$ does not diminish the strength of an acid. The difference can only be understood by assuming that, in the case of the former class of acids, the nitrogen of the basic group, $-R'''NH_2$, is in combination with the hydrogen of the acid group, $-CO_2H$ or $-SO_3H$; thus—

$$\underline{H_3N \cdot R'' \cdot CO} \cdot \underline{O}, \; or \; \underline{H_3N \cdot R'' \cdot SO_2} \cdot \underline{O},$$
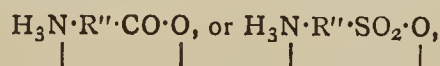
the dissociation of these molecules into H, on the one hand, and—

$$\underline{H_2N \cdot R'' \cdot CO} \cdot \underline{O}, \; or \; \underline{H_2N \cdot R'' \cdot SO_2} \cdot \underline{O},$$
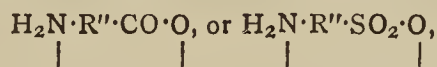
on the other, occurring to a much less extent than in the case of the non-amidated acids, which dissociate into H and $R' \cdot CO_2$ or $R' SO_3$.

Finally, the author considers the dilution formulæ of electrolytes recently proposed by Rudolphi (*Zeit. Phys. Chem.*, 1895, xvii., 385) and van 't Hoff (*Zeit. Phys. Chem.*, 1896, xviii., 300), and shows that his results are in agreement with these formulæ.

**132.** "*The Physiological Action of Amidosulphonic Acid.*" By OSCAR LOEW, Ph.D.

Amidosulphonic acid, applied as its calcium or sodium salt, proves to be noxious to the life of phænogamous plants, but not to Algæ or to the lower Fungi. It is not poisonous to the lower aquatic forms of animal life, such as Infusoria, Rotatoria, Copepoda; and, from experiments made by Prof. D. Takahashi, it proves to be also not poisonous to vertebrate animals, such as the dog and the frog. That its poisonous action should be confined to flowering plants is a point of much interest.

**133.** "*How Mercurous and Mercuric Salts change into each other.*" By S. HADA, B.Sc.

By the results of numerous experiments, the ways are shown by which mercuric salts in presence of water become mercurous, and mercurous salts become mercuric. Very much has been observed already by others concerning such a common subject, but the statements based on past experience have been uncertain and even contradictory, and nearly every point has had to be worked out anew.

It has now been ascertained that a cold solution of mercuric nitrate shaken with mercury is at once and fully converted into one of mercurous nitrate, one of mercuric acetate into mercurous acetate, and one of mercuric chloride into simple water and a precipitate of mercurous chloride. As was better known, moist mercuric sulphate or phosphate quickly becomes all mercurous salt, with evolution of heat, when rubbed with mercury.

Mercurous nitrate in boiling water becomes mercuric nitrate and metallic mercury, which distils with the steam. Other mercurous salts, soluble or insoluble, e. g., the chloride, behave similarly. This dissociation proceeds also at lower temperatures, even to a measurable extent at 40°, in the case of the nitrate, on condition that, by a current of air, the mercury vapour is carried away.

Mercurous salts, in solution or moist, are also all dissociated at the common temperature by strong daylight, the acetate allowing the effects of dissociation to be very clearly observed.

Mercurous nitrate, when free from its mother-liquor, is a stable salt, unchanged in the air if not exposed to bright light. In solution in the dark, in a closed vessel, it is also stable even in an atmosphere of oxygen. There is no evidence that this or any other mercurous salt, whether in solution or only moist, is oxidisable in the air at common or only moderately elevated temperatures. What has been supposed to be the effect of oxidation, as in Mialhé's experiments, is the effect of dissociation. Mercurous oxide alone is oxidisable.

Mercurous salts, in presence of water, and best when in solution, oxidise in air or oxygen at a temperature of 150°. Thus, mercurous chloride can be largely, if not wholly, changed by oxidation into mercuric chloride in presence of hydrochloric acid. When mercurous chloride, boiled with hydrochloric acid under atmospheric pressure, becomes mercuric chloride, it does so by dissociation, not by appreciable oxidation.

Mercurous nitrate in water at the common temperature, but in strong daylight, becomes mercuric salt by reduction of its own nitric acid to nitrous acid. Exposure in an open vessel, or to an atmosphere of mercury vapour, or even to undiluted oxygen, retards the progress of the change by keeping down the quantity of nitrous acid which otherwise increases with time. An atmosphere of carbon dioxide favours—that is, does not impede—the change.

Mercurous nitrate also freely becomes mercuric nitrate and nitrite when kept in solution at 150° under pressure.

Mercurous oxide both oxidises and dissociates at the common temperature, as has been shown by Barfoed. Exposed to the air, it increases or lessens in weight, according to conditions. Shut up in an atmosphere of moist air, it gains in weight, dissociation being checked and oxidation favoured. Exposed with large surface to the open air, it loses in weight, for then dissociation and volatilisation of the mercury go on faster than oxidation of the undecomposed mercurous oxide.

134. "*The Effect of Heat on Aqueous Solutions of Chrome Alum.*" By MARGARET D. DOUGAL.

As is well known, the colour of an aqueous solution of chrome alum, when heated, changes from violet or purple to green, and, on evaporating, the green solution yields a green non-crystalline mass.

The author has made a series of observations on the relative rates of diffusion of green and violet solutions of the same initial strength, which go to prove that the green diffusate contains less chromium and more sulphuric acid than the violet diffusate, which is compatible with the assumption that the green solution contains a colloidal, and therefore slowly diffusing chromosulphuric acid. This conclusion is in harmony with the results recently arrived at by Monte, and inferred by Whitney, that when a solution of chrome alum is heated it is resolved into a mixture of potassium sulphate, chromylsulphuric

acid, and free sulphuric acid, according to the following equation :—

$$2[Cr_2(SO_4)_3 K_2SO_4] + H_2O =$$
$$= [Cr_4O(SO_4)_4]SO_4 + 2K_2SO_4 + H_2SO_4.$$
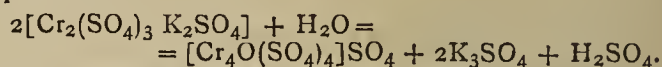
Experiments have also shown that solutions of chrome alum, after heating, are less dense than the unchanged or violet solutions, the expansion being due, in all probability, to the production of the free sulphuric acid.

135. "*On the Hydrolysis of Ethylic Dicarboxylglutaconate.*" By H. W. BOLAM, B.Sc., Ph.D.

It was found impossible to prepare glutaconic acid in quantity from ethylic dicarboxylglutaconate, following the directions of Conrad and Guthzeit (*Annalen*, ccxxii., 254). Attempts to prepare this acid from β-oxyglutaric acid likewise failed. No oxyglutaric acid, such as v. Pechmann and Jenisch (*Ber.*, 1891, xxiv., 3250) describe, could be isolated from the product of the reduction of acetone-dicarboxylic acid by means of sodium amalgam.

It was found that ethylic dicarboxylglutaconate underwent, on boiling with alkalis (baryta and caustic potash), a remarkable decomposition, the products being malonic acid and formic acid. The yields of glutaconic acid are still further reduced by the action of alkali, it being shown that oxyglutarates (possibly β-) are formed. The decomposition is effected on boiling with a *one* per cent solution of baryta ; in the cold, on the other hand, no such decomposition was observed with even a 20 per cent solution of caustic potash. On saponifying the ethylic dicarboxylglutaconate with acids no such decomposition takes place ; here, however, syrupy products, presumably both α- and β-oxyglutaric acids and the lactone acid, butyrolactone carboxylic acid, are formed, and these hinder the crystallisation of the glutaconic acid. Using 11 per cent hydrochloric acid, and observing certain precautions in boiling, and on evaporation, yields of from 50 to 60 per cent of glutaconic acid are got.

Ethylic benzyldicarboxylglutaconate undergoes no decomposition on boiling with alkalis, nor does the benzylglutaconic acid thus formed show any tendency to form oxy-acids. It is supposed that other alkyl substituted ethylic dicarboxylglutaconates behave similarly, and it is suggested that an explanation of the decomposition of the simple ethylic dicarboxylglutaconate is to be found in the presence of the hydrogen atom replaceable by a metal, and that, further, only ethers having such a replaceable hydrogen atom may be expected to show an analogous decomposition on boiling with alkalis.

136. "*The Periodic Law.*" By R. M. DEELEY.

In this paper it is pointed out that the manner in which the elements group themselves varies according to the comparative importance which is attached to their several physical and chemical properties. The elements have generally been grouped in accordance with their most striking chemical properties. When thus grouped the author shows that many of them do not fall in with a regular periodic system, and the arrangement would seem to indicate that quite a number of elements of small atomic weight remain to be discovered. On the other hand, when they are grouped in accordance with the periodic changes in the values of many of their physical properties, the result is much more satisfactory. As an example, the refraction equivalents are instanced, helium being shown to fill a blank for a missing element (pointed out in a previous paper), whilst argon falls most naturally between sodium and fluorine. The periodic arrangement proposed makes the list of elements of smaller atomic weight than iodine complete, if we discount the possibility of the existence of a whole group of inert elements of lower atomic weights respectively than hydrogen and the alkali metals.

137. "*The Colouring-matters occurring in various British Plants.*" Part I. By A. G. PERKIN and J. J. HUMMEL.

Formerly numerous British plants were employed in

dyeing, and at present in remote districts, notably the Highlands of Scotland, some are still used for this purpose. Many of these have been found sufficiently strong in colouring-matter to warrant their chemical examination.

*The colouring-matters of the yellow wallflower*, Cheiranthus cheiri.—An aqueous extract of the flowers when digested with acid deposits a precipitate of colouring-matter; this was found to consist of two substances which could be separated readily, owing to the difference of their solubilities in alcohol. The *more soluble* product which was obtained as yellow needles, had the formula $C_{15}H_{10}O_7$, yielded an acetyl compound,—

$$C_{15}H_5O_7(C_2H_3O)_5;$$
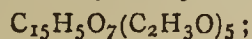
colourless needles, m. p. 189—191°; when decomposed with fused alkali, protocatechuic acid and phloroglucin were produced. It was found to be *quercetin*.

*The sparingly soluble colouring-matter*, $C_{16}H_{12}O_7$, minute, yellow needles, gave an acetyl compound, colourless needles, melting at 195—196°, and, when acted upon by hydriodic acid, it yielded *quercetin*, and one molecule of methylic iodide. It was thus a *quercetin monomethyl ether*. Though closely resembling rhamnetin it is not identical with it, for acetylrhamnetin melts at 184—185°; and for it is proposed the name *isorhamnetin*.

*The colouring-matter in white hawthorn blossoms*, Cræ-tagus oxycantha, was obtained as yellow needles having the formula $C_{15}H_{10}O_7$. Its acetyl compound, colourless needles, melted at 189—191°, and, when fused with alkali, phloroglucin and protacatechuic acid were formed. There could be no doubt as to its identity with *quercetin*. It is most probable that these colouring-matters exist in the above plants as glucosides. This point will be studied at a later date.

138. "*Position-isomerism and Optical Activity; the Comparative Rotatory Powers of the Dibenzoyl and Ditoluyltartrates.*" By PERCY FRANKLAND, Ph.D., F.R.S., and FREDERICK MALCOLM WHARTON, A.I.C.

The authors have recently shown (*Trans.*, 1896, 1309) that the rotatory effect of the para-toluyl radicle is greater than that of the meta- and this again greater than that of the ortho-toluyl group. This relationship, they have pointed out, is in harmony with the relative position of the centre of gravity in these several groups, for assuming that the centre of gravity of the benzene ring is the geometrical centre of a regular hexagon, it is obvious that in the ortho-arrangement of the toluyl group the centre of gravity is somewhat nearer, in the meta-arrangement somewhat further, and in the para-arrangement still further than that geometrical centre from the carbonyl carbon atom by means of which the ring is in each case attached to the asymmetric carbon atom of the tartaric acid. They have now investigated the relationship subsisting between the rotation of these toluyl compounds and the corresponding benzoyl derivatives. To this end they have studied the rotation, over a wide range of temperature, of methylic and ethylic dibenzoyltartrate, with the result that they have found that the rotation of the benzoyl compound is in each case intermediate between that of the corresponding ortho- and meta-toluyl derivative. This is also the relative position of the centre of gravity in the respective rings with regard to the carbonyl carbon atom by means of which they are attached.

Methylic and ethylic dibenzoyltartrates, like the corresponding ditoluyltartrates, were found to possess rotations which are very sensitive to temperature, the high negative value of the rotation diminishing with rise of temperature. In this condition ethylic dibenzoyltartrate was found to exhibit the phenomenon of a maximum rotation. This maximum is situated in the vicinity of its melting-point, the rotation values diminishing more and more as it is examined in a state of superfusion at temperatures further and further below its melting-point.

139. "*Researches on the Terpenes. VII. Halogen Derivatives of Camphor.*" By J. E. MARSH and J. H. GARDNER.

When camphor is treated with a mixture of bromine and phosphorus trichloride at the ordinary temperature, it yields a mixture of two isomeric compounds, of the formula $C_{10}H_{14}Br_4$, α- and β-tribromocamphene hydrobromides. The two compounds are separated by crystallising from light petroleum.

α *Tribromocamphene hydrobromide* crystallises from chloroform in large colourless crystals; it melts at 168°, and its specific rotatory power $[a]_D = + 90.3°$.

β-*Tribromocamphene hydrobromide* melts at 143—144°, and has the rotatory power $[a]_D = + 7.6°$.

When boiled with sodium methylate in methyl alcohol both the above-mentioned compounds react in the same way, losing hydrobromic acid, and yielding the same *tribromocamphene*, $C_{10}H_{13}Br_3$.

Tribromocamphene melts at 75—76°, and has the specific rotatory power $[a]_D = + 33.5°$.

The action of bromine and phosphorus trichloride on other substances has been examined. Borneol yields the same compound (m. p. 168°) as camphor. Ordinary turpentine gives a new compound of the formula $C_{10}H_{14}Br_6$, which crystallises in colourless needles melting at 150°.

When pentachloride of phosphorus acts on camphor in the cold, two isomeric chlorocamphene hydrochlorates are obtained, which may be separated by petroleum ether. One of these compounds, α-*chlorocamphene hydrochloride*, appears to be in all respects identical with that originally described by Spitzer, having the melting-point 155° and specific rotatory power $[a]_D = - 9°$.

β-Chlorocamphene hydrochlorate is very slightly soluble in petroleum ether, and crystallises from the hot solution in large, colourless, hard crystals; that obtained by Spitzer forms small, soft, binding crystals. The new isomeride melts at 168°, and has the rotatory power $[a]_D = - 27.7°$. When boiled with zinc dust and glacial acetic acid it yields *chlorocamphene*, $C_{10}H_{15}Cl$, a colourless solid of low melting-point, which distils at 202° and has a specific rotatory power $[a]_D = - 29.7°$.

Spitzer's compound also yields a chlorocamphene by the same treatment, but it is difficult to say whether it is identical with or different from the derivative of the β-compound. It is usually contaminated with higher chlorinated products.

When chlorocamphene is acted on with strong sulphuric acid it dissolves, with evolution of hydrogen chloride, and on pouring the solution into water a liquid is obtained, which can be distilled in steam. It has a strong camphorous smell, and burning taste. It boils at 250°, and has the composition $C_{10}H_{16}O$. The examination of its properties is not completed, but it appears to be a saturated tertiary alcohol, and is probably a hydroxyl-derivative of camphene.

140. "*Derivatives of Camphenesulphonic Acids.*" By ARTHUR LAPWORTH, D.Sc., and FREDERIC STANLEY KIPPING, Ph.D., D.Sc.

This paper contains an account of the study of the two camphenesulphonic chlorides which are obtained as by-products in the preparation of camphorsulphonic chloride; the properties of these substances, and those of all their more important derivatives, have been briefly described in previous notes (*Proc.*, 1895, 57; 1896, 152).

141. "*Preparation of Dimethylketohexamethylene and Experiments on the Synthesis of Dimethylhexamethenyl-malonic Acid.*" By F. STANLEY KIPPING, Ph.D., D.Sc., and W. B. EDWARDS.

The appearance of a paper by Verwey on "Penta-methenylmalonic Acid and Pentamethenylacetic Acid," in a recent number of the *Berichte* (xxix., 1996) has led us to take the earliest opportunity of making known the results of some experiments which were commenced last spring, and which were undertaken, partly with the object

of synthesising dimethylhexamethenylmalonic acid and dimethylhexamethenylacetic acid—homologues respectively of the compounds derived by Verwey—and partly with the object of making a general study of hexamethylene derivatives.

To obtain these substances it was necessary to prepare dimethylketohexamethylene (*Trans.*, 1895, 349), and for this purpose a large quantity of dimethylpimelic acid was required; in the first place, therefore, we endeavoured to find a better method for preparing this acid than the one previously adopted (*Trans.*, 1891, 569), and this we accomplish in the following manner:— The acetyldimethylcaproic acid which is formed, together with dimethylpimelic acid, by the hydrolysis of ethylic dimethyldiacetylpimelate (*loc. cit.*) is dissolved in excess of aqueous sodium hydroxide and bromine is then added, in small quantities at a time, until bromoform is no longer produced; under these conditions the acetyldimethylcaproic acid seems to be converted quantitatively into dimethylpimelic acid.

This fact being established, the crude mixture of acids directly obtained from ethylic dimethyldiacetylpimelate may be submitted to oxidation in the above manner, the troublesome separation of the two acids thus being avoided.

Having prepared a considerable quantity of dimethyl pimelic acid in this way, we converted it into dimethylketohexamethylene by distilling its barium salt and reduced the ketone with sodium in moist ethereal solution thus obtaining the corresponding alcohol, which has been recently described by Zelinsky; this alcohol was then converted into dimethylhexamethylene bromide by treating it with hydrobromic acid.

We then began to study the conditions under which ethylic dimethylhexamethenylmalonate could be prepared by the interaction of dimethylhexamethylene bromide and ethylic sodiomalonate, but the experiments were interrupted by the summer vacation, and have not yet been resumed; as, however, they will be continued at an early date the publication of this note seemed desirable.

The fact that Noyes (*Ber.*, 1896, 2326) has lately obtained from dihydrocampholytic acid (*cis*) a ketone which may be identical with dimethylketohexamethylene, enhances the interest which is attached to the further study of this compound.

(To be continued).

## PHYSICAL SOCIETY.

*Special General Meeting, November 27th, 1896.*

Captain ABNEY, President, in the Chair.

THE Resolutions passed at the Special General Meeting held on October 30th were confirmed.

*Ordinary Meeting.*

Prof. RÜCKER, Vice-President, in the Chair.

The President (Captain ABNEY) described and exhibited some Apparatus for giving Diagrams of the Efficiency of a Photographic Shutter.

In addition to the "speed" of a shutter, which is concerned with the interval (T) between the moments when the shutter admits *the first* and *last* rays of light, it is most important to know the efficiency of the shutter. The efficiency may be defined as follows:—Let $x$ represent the portion of the available aperture of the lens exposed by the shutter at a time $t$, and let X be the total available aperture. Then, if the shutter were perfectly efficient, *i.e.*, if the whole of the aperture were efficient during the time T, the quantity of light admitted would be proportional to X T. In other cases the quantity of light admitted will be proportional to—

$$\int_0^T x\, dt.$$

Hence the efficiency is—

$$\frac{\int_0^T x\, dt}{X\,T}.$$

The apparatus employed by the author consists of a slit placed near the shutter, so that the length of the slit is at right angles to the direction of motion of the shutter, and a lens, by means of which an image of the slit is thrown on to a rotating drum or plate. The slit, when the shutter is open, is illuminated by the light of an arc lamp, a condensing lens being employed. In order to obtain a time scale two devices have been employed. In one of these a spoked wheel is rotated at a known speed, so that each spoke, as it passes, momentarily cuts off the light. In the other arrangement a small lens, attached to the prong of a tuning-fork, throws a small spot of light on to the rotating drum, and thus gives a wavy line. Bromide paper or celloidin films are employed to record the diagrams.

If the shutter were perfectly efficient the diagram would consist of a rectangle, crossed, if the rotating wheel is used, by a number of white lines, caused by the interruption of the light by the spokes of the wheel. These lines give a time scale by which the speed of the shutter can be calculated.

The author showed a number of diagrams taken by the apparatus, and illustrating the behaviour of different shutters under varying conditions. In one of these the rebound of the shutter at quick speeds is clearly shown by each of the principal diagrams being followed by a small auxiliary one.

Prof. PERRY said he supposed that what was required was some method of showing the *motion* of the shutters.

Mr. BOYS suggested that the efficiency might be defined as the ratio of the area of the actual diagram to that of the rectangle having as base the time between the commencement and end of the exposure.

Mr. INWARDS asked if the author had made any experiments to determine the amount of shake communicated to the camera by the motion of the shutter.

Prof. PERRY said what was required was an exceedingly light shutter that got up a great speed before it reached the aperture.

The Author, in his reply, said he had investigated the question of the shake due to the movement of the shutter. He considered that the amount of this shake depended upon the extent of the movement of the centre of gravity of the shutter. With a small stop the Thornton-Picard shutter fulfilled Prof. Perry's requirements. The experiments have shown that the exposure does not always vary as the square of the aperture, on account of the small efficiency of some shutters for oblique rays. Thus in one case by doubling the aperture you only increase the light threefold.

The Society then adjourned till December 11th.

## NOTICES OF BOOKS.

*Hygienic Review of Chile.* Vol. ii., No. 6. ("Revista Chilena de Higiene").

THE issue before us contains a paper on the bacteriological analysis of atmospheric dust, by Dr. Mamak Cádiz,—a summary of opinions in favour of and hostile to the Vitacuna water supplied to Santiago, from which we quote merely the damnatory fact that it contains, per 1000 grms., 866 m.grms. of lead; and a series of clinical

observations on serotherapy, as applied in the treatment of cancer.

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*A Junior Course of Practical Chemistry.* By FRANCIS JONES, F.R.S.E., F.C S., Chemical Master in the Grammar School, Manchester. With a Preface by Sir H. E. ROSCOE, F.R.S. London and New York: The Macmillan Co. (Ltd.). 1896.

THIS work is now in its eighth edition, and calls for little comment. Its teachings are correct, like those of very many other chemical manuals. It is arranged to suit the new Syllabus of the Science and Art Deparment, and is fitted up with an Appendix of questions and exercises.

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# CORRESPONDENCE.

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## COTTON SEEDS.

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*To the Editor of the Chemical News.*

SIR,—Will you permit me to add a word to the letter of Dr. George F. Payne, published in the CHEMICAL NEWS of October 16th (lxxiv., p. 196).

It is rather curious that Dr. Blyth should not have been acquainted with the nature of the poisonous bases which are present sometimes in cotton seeds. The poisonous nature of these bases was first pointed out by Böhm in 1881, who discovered cholin in cotton seed. The presence of betain in the same substance was pointed out by Ritthausen and Weger in 1882. The fact that cholin was more poisonous than betain was subsequently determined by physiological experiments conducted by Gaehtgens. A thorough study of these nitrogenous bases in cotton seeds has been made in this laboratory by Maxwell and the results published in the *American Chemical Journal*, vol. xiii., p. 469. In the third volume of my work on the "Principles and Practice of Agricultural Analysis," p. 429, occur the following sentences :—

"These bodies (viz., cholin, betain) have acquired an economic interest on account of their occurrence in cotton seed meal, which is so extensively used as a cattle food. It is evident from the relative proportions in which they occur that the less nocuous base, betain, is the more abundant. It is possible, however, that the base originally formed is cholin and that betain is a secondary product. Experience has shown that it is not safe to feed cotton seed meal to very young animals, while moderate rations thereof may be given to full-grown animals without much expectation of deleterious results. In the case of toxic effects it is fair to presume that a meal has been fed in which the cholin is relatively more abundant than the betain."

The methods used in this laboratory for detecting, isolating, and separating the two bases are fully described on pp. 428-29 of the work referred to.—I am, &c.,

H. W. WILEY,
Chief of Division.

United States Department of Agriculture,
Div. of Chemistry, Washington, D.C.,
November 16, 1896. .

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# CHEMICAL NOTICES FROM FOREIGN SOURCES.

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NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

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*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 19, November 9, 1896.

M. Berthelot presented to the Academy a work which he has just published under the title "Science and Morals."

It contains various articles and discourses on the general part played by Science in Society and Education. It contains also biographical notices of Pasteur, Cl. Bernard, and P. Bert, and articles on the History of the Sciences, *e.g.*, on the discovery of alcohol, on the preservation of ancient industries, on the chemistry of the Arabs, &c.

Composition of the Fruits of Phœnix melanocarpa. —Aimé Girard.—This fruit is a species or variety of date. Its saccharine matter consists entirely of levulose. It contains neither acids nor tannic matters, but abounds in pectine.

Action of Aluminium Chloride upon Camphoric Anhydride.—G. Blanc.—Not suitable for abstraction.

On the Essential Oil of Resin.—Eugene Charabot and G. Chiris.—The rotatory power of French oils is stronger than that of Turkish samples.

New Ferment in the Blood.—M. Hanriot.—This ferment, which the author names lipase, is very stable and acts principally upon fatty matters.

Chemical Method of Appreciating the Value of Wheat Flours from the Baker's point of view.—E. Fleurent.—The author finds that gluten may be divided into three classes : — 1. Glutens which are decidedly elastic ; 2. Drier and more brittle glutens, easily desiccated and more frangible ; 3. Very tender glutens, easily elongated but scantily elastic. These differences are due to the different proportions of glutenine and gliadine in the glutens examined.

Application of the Röntgen Rays in Palæontology. —M. Lemoine.—The author finds that the X rays easily traverse the fossilised walls of bony pieces, apparently very opaque. This method will in many cases be an improvement on the use of sections.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Parts 4 and 5.

Reactions for Glucose, Aldehyds, and Ketones.— A. Jaworowski (*Pharm. Post* and *Pharm. Central Halle*). —Orthonitrophenol, like picric acid, if heated with an alkaline solution of glucose, produces a brown colouration. Commercial nitrobenzol, under similar conditions, colours a solution of glucose at first red and then a dirty brown. If 3 c.c. of dilute sulphuric acid are mixed with 0·1 grm. of sodium vanadiate, and then superstratified with solution of glucose, there appears a green or blue ring. If solution of glucose is boiled with a little iodic acid and soda lye, the liquid acidulated when cold, and superstratified with ammonia, there is formed a dark precipitate (nitrogen iodide). If solution of glucose is heated with Jaworowski's ammonia test (1 part mercuric chloride, 1 part sodium carbonate, 4 parts sodium chloride, 30 parts water), there is formed a yellow precipitate, afterwards turning grey. A similar reaction occurs with the Nessler test (the precipitate being at first reddish brown, then brown, dirty green, and at last grey). All these reactions hold good for the aldehyds and ketones, excepting the iodic acid reaction.

A Boiling Flask, consisting in its lower part of milk-glass, is proposed by H. M. Smith (CHEMICAL NEWS) for determining sugar with Pavy's solution.

An Electric Blowpipe. — H. N. Warren (CHEMICAL NEWS).

Determination of the Halogens.—A series of notes from different authorities.

Behaviour of Tartaric Acid and its Alkaline Salts with certain Agents.— Magnier de la Source (*Comptes Rendus*).

Reactions of Formal Aldehyd.—T. H. Lee.—(From the CHEMICAL NEWS).

## MISCELLANEOUS.

**Forthcoming Books.**—We learn from Mr. Hart, of the Chemical Publishing Co., Lafayette Press, Easton, Pennsylvania, that they will shortly bring out an important chemical work by Dr. Wiley in three volumes, and one by T. S. Stillman on Engineering Chemistry. Our readers may be interested in knowing that the staff at Mr. Hart's office consists entirely of chemists, thereby helping to approach the ideal in publishing chemical books.

**The Royal Society.** — The following Officers and Members of Council were elected November 30, 1896 :—
*President.*—Sir Joseph Lister, Bart., F.R.C.S., D C.L.
*Treasurer.*—Sir John Evans, K.C.B., D.C.L., LL.D.
*Secretaries.*—Prof. Michael Foster, M.A., M.D., D.C.L., LL.D.; Prof. Arthur William Rücker, M.A., D.Sc.
*Foreign Secretary.*—Edward Frankland, D.C.L., LL.D.
*Other Members of the Council.*—Prof. William Grylls Adams, M.A.; Prof. Thomas Clifford Allbutt, M.D.; Prof. Robert Bellamy Clifton, M.A.; William Turner Thiselton Dyer, C.M.G.; Prof. James Alfred Ewing, M.A.; Lazarus Fletcher, M.A.; Walter Holbrook Gaskell, M.D., Prof. Alfred George Greenhill, M.A.; William Huggins, D.C.L.; Prof. Charles Lapworth, LL.D.; Major Percy Alexander MacMahon, R.A.; Prof. Raphael Meldola, F.C.S.; Prof. William Ramsay, Ph.D.; The Lord Walsingham, M.A.; Prof. Walter Frank Raphael Weldon, M.A.; Admiral William James Lloyd Wharton, C.B.

## MEETINGS FOR THE WEEK.

MONDAY, 7th.—Society of Arts, 8. "The Use of Gas for Domestic Lighting" (Cantor Lectures), by Prof. Vivian B. Lewes.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "The Alkali Manufacture—An Historical Sketch," by Alfred E. Fletcher. ' Notes on the Spontaneous Oxidation of Aluminium in contact with Mercury,' by H. F. Hunt and L. J. Steele.
WEDNESDAY, 9th.—Society of Arts, 8. "Mining at Great Depths," by Bennett H. Brough, Assoc. R.S.M.

## THE BRISTOL GAS COMPANY.

### TENDER FOR TAR.

The Directors of this Company invite Tenders for the Purchase of the TAR to be produced at all or either of their three Stations during a period of One, Two, or Three Years, commencing on the 1st day of January, 1897.
The annual quantities of Tar produced at each of the Stations at present are, approximately, as follows :—

| | |
|---|---|
| Avon Street .. .. .. .. | 650,000 gallons |
| Canons' Marsh .. .. .. | 550,000 ,, |
| Stapleton.. .. .. .. .. | 650,000 ,, |

Further particulars, with Forms of Tender, may be obtained on application to the undersigned, to whom also Tenders sealed, and endorsed "Tender for Tar," must be delivered not later than WEDNESDAY, the 9th day of December proximo.
                                        JOHN PHILLIPS, Secretary.
Chief Offices, Canons' Marsh,
November 26, 1896.

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1932.

## THE ANALYSIS OF "CAP COMPOSITION."

By F. W. JONES and F. A. WILLCOX, B.Sc.

"CAP composition" usually consists of the ingredients potassium chlorate, antimony sulphide, and mercury fulminate, and to estimate these substances in the presence of each other by ordinary analytical methods is a difficult process, since the separation of antimony sulphide and mercury fulminate in the presence of potassium chlorate necessitates the treatment of the mixture with hydrochloric acid, and this produces an evolution of sulphuretted hydrogen from the sulphide, and a consequent precipitation of sulphur; and potassium chlorate cannot be separated from the other ingredients by treatment with water, owing to the appreciable solubility of mercury fulminate in cold water.

We observed in the course of some experiments on the solubility of mercury fulminate that this body was readily soluble in acetone and other ethereal solvents when they were saturated with ammonia gas, and that potassium chlorate and antimony sulphide were insoluble in pure acetone saturated with ammonia: and these observations at once afforded a simple method of separating the three ingredients of cap composition. By employing this solution of acetone and ammonia an analysis can be made in a comparatively short time, and yields results of sufficient accuracy for all technical purposes.

The following are the details of the analysis:—A tared filter-paper is placed in a funnel, to the neck of which has been fitted a piece of rubber tubing provided with a clip. The paper is moistened with the solution of acetone and ammonia; the cap composition is weighed off directly on to the filter-paper, and is then covered with the solution of acetone and ammonia, and allowed to stand for three or four hours. It is then washed repeatedly with the same solution until the washings give no colouration with ammonium sulphide, and afterwards washed with acetone until the washings give no residue on evaporation, dried, and weighed.

The paper is again put in the funnel, and washed with water until free from potassium chlorate, dried, and weighed.

If $c$ = weight of composition taken,
$d$ = weight of filter-paper,
$a$ = weight after first extraction,
$b$ = weight after second extraction;

then $c + d - a$ = weight of fulminate of mercury,
$c + d - a - b$ = weight of potassium chlorate,
$b - d$ = weight of antimony sulphide.

The results of the analyses, by this method, of two mixtures of known composition are given below:—

|  | A. | | B. | |
| --- | --- | --- | --- | --- |
|  | Percentage taken. | Percentage found. | Percentage taken. | Percentage found. |
| Antimony sulphide | 36.47 | 36.25 | 37.34 | 37.22 |
| Potassium chlorate | 33.25 | 33.71 | 46.03 | 46.43 |
| Mercury fulminate | 30.27 | 30.02 | 16.61 | 16.34 |

It is necessary, in carrying out an analysis, to previously grind the composition in an agate mortar (of course with due care, and taking only small quantities at a time), and to dry the filter-paper always at the same temperature.

## FILTER FLASK.

### By W. DIAMOND.

I HAVE enclosed a rough drawing of what I think a decided improvement on the filter-pump flask in general use. The shape and use of the ordinary one we all know. My improvement is as follows:—

Instead of the flask being flat-bottomed I have it made dome-shaped, at the bottom of which there is a tap, B, which acts as an outlet. Close to the neck there is another tap, A, but a very small one, which breaks the vacuum when turned on. The whole is supported upon a tripod, the flask having tabs projecting which rest upon the rim of the tripod.
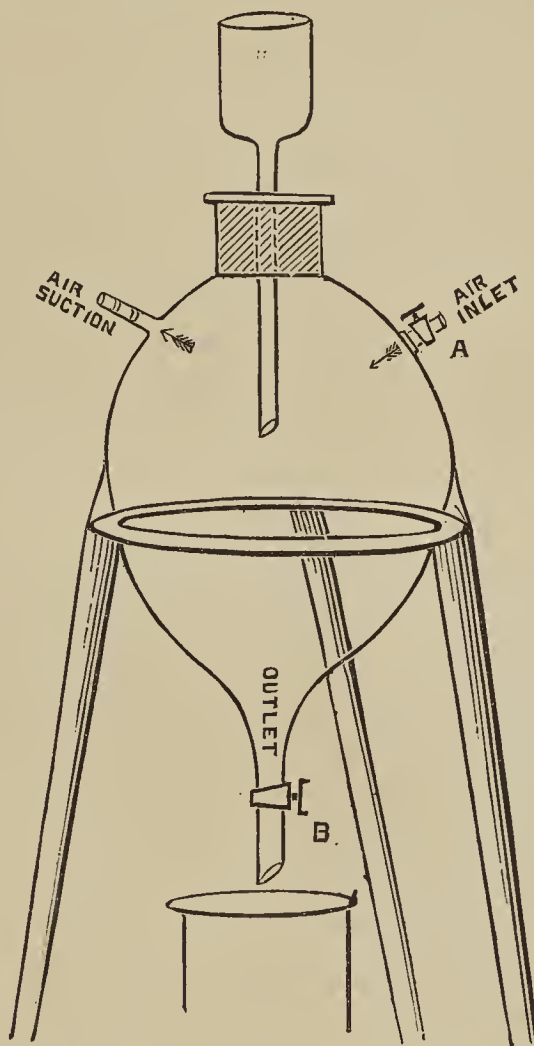


This apparatus saves a lot of unnecessary work. If a chemist or a student has a large volume of liquid to filter, perhaps he may have to detach the cork and funnel from the neck several times in course of filtration, which also incurs the possibility of losing a portion of the precipitate or residue from the filter by jarring. These difficulties are somewhat alleviated by my apparatus. To dispense with the filtrate the air-tap, A, is turned on, thus allowing a current of air to get into the flask and breaking the vacuum; then the outlet-tap, B, may be turned on, and so run the liquid away; when empty turn the taps off, and all is again working.

Chemical Works Laboratory, Pye Bridge,
November 24, 1896.

Reactions of Gallic Acid, Tannin, Pyrocatechin, and Protocatechuic Acid. — F. Koch (*Archiv der Pharmacie*).—The reagents are solutions of ferric chloride at $\frac{1}{2}$, 1, 2, and 4 per cent, and $\frac{1}{2}$ per cent solution of sodium bicarbonate. A drop of the solution of ferric chloride is first added and then the sodium bicarbonate solution is added drop by drop until the full colour is produced.

# IODOMETRIC DETERMINATION OF SELENIOUS AND SELENIC ACIDS.*

## By JAMES F. NORRIS and HENRY FAY.

THE methods already in use for the volumetric determination of selenious acids are those of Muthmann and Schaefer (*Ber. d. Chem. Ges.*, xxvi., 1008), and Gooch and Peirce (*Am. J. Sci.*, i. [4], 31). The former method has been studied by Gooch and Reynolds (*Ibid.*, xxx., 254), and found to be inaccurate. The method of Gooch and Peirce depends upon the reduction of a known weight of potassium iodide in sulphuric acid solution by selenious acid in presence of arsenic acid. The difference between the arsenious acid equivalent to the potassium iodide and the amount found, is a measure of the selenious acid. Selenic acid is first reduced by boiling with potassium bromide and sulphuric acid under definite conditions.

The method here proposed requires fewer reagents, occupies less time, and gives more accurate results. The determination depends on the reaction between sodium thiosulphate and selenious acid in presence of hydrochloric acid. So far we are unable to state the complete reaction which takes place, but have found that 1 molecule of selenious acid is exactly equivalent to 4 molecules of sodium thiosulphate. After standing about twenty-four hours, part of the selenium is precipitated. In neutral solution the reaction takes place slowly, and is not complete after standing a day. In a strong neutral solution there is immediate precipitation of selenium, and the reaction becomes strongly alkaline. In this solution no sulphates were found. It is proposed to make a more complete study of this reaction.

The reagents used were carefully purified. Re-sublimed iodine was sublimed from one-third of its weight of potassium iodide, and dissolved in potassium iodide free from iodate. This precaution was necessary, as the titrations were made in acid solution. A hot concentrated solution of potassium iodide was boiled five minutes with the addition of a small quantity of hydrochloric acid, the solution cooled rapidly, and the precipitate washed with alcohol to remove free iodine. The potassium iodide gave no reaction with starch when acidified with hydrochloric acid.

As the commercial sodium thiosulphate gave a different iodine-value in acid and neutral solution, it was found necessary to re-crystallise it to remove the sulphite, although the presence of the latter was not indicated by barium chloride. The sodium thiosulphate was standardised against re-sublimed iodine and pure sodium arsenite,

The selenious acid was prepared from commercial selenium by evaporating to dryness with concentrated nitric acid. The selenium dioxide thus obtained was reduced by sodium sulphite and hydrochloric acid, and the pure selenium was again oxidised by evaporating to dryness with nitric acid, and the residue re-sublimed. In order to prevent reduction the oxide was sublimed in a small beaker, covered with a watch-glass, and containing a drop of strong nitric acid. By this method long, perfectly white, needles of selenium dioxide can be obtained which are free from selenic acid. About 2 grms. were weighed accurately, dissolved in water, and diluted to 500 c.c.

The selenic acid was prepared by dissolving about 2 grms. of selenium dioxide in 200 c.c. of water, and adding a strong solution of potassium permanganate until a permanent pink colour remained after heating one-half hour at 60° C. Sulphurous acid was then added until only a small amount of manganese dioxide remained, and the solution filtered and diluted to 500 c.c. Sodium thiosulphate titrated in the presence of a definite portion of this solution, acidified with hydrochloric acid,

gave the same iodine-value as without its presence, thus showing the absence of selenious acid.

The flasks and burettes were calibrated according to the method of Morse and Blalock (*Amer. Chem. Journ.*, xvi., 479).

## Determination of Selenious Acid.

A definite portion of selenious acid was measured off, diluted with ice-water and 10 c.c. hydrochloric acid (1·12 sp. gr.). An excess of one-tenth normal solution of sodium thiosulphate was added and titrated back with iodine solution. One molecule selenious acid, $SeO_2$, is equivalent to 4 molecules of thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$. It was found necessary to have enough hydrochloric acid present to set free all of the thiosulphuric acid. If the solution is cold, a large excess of hydrochloric acid does not affect the titration. The following is a series of eight consecutive determinations :—

| $SeO_2$ taken. | $SeO_2$ found. | $SeO_2$ taken. | $SeO_2$ found. |
|---|---|---|---|
| 0·0829 | 0·0829 | 0·1366 | 0·1367 |
| 0·0829 | 0·0829 | 0·1366 | 0·1368 |
| 0·1242 | 0·1242 | 0·1656 | 0·1659 |
| 0·1242 | 0·1242 | 0·2070 | 0·2071 |

It will be seen that the error varies from 0·00 to 0·18 per cent, the average being 0·06 per cent. The method is therefore one of the most accurate of iodometric methods and can be used conveniently for the standardisation of sodium thiosulphate. The solution of selenious acid is entirely stable.

## Determination of Selenic Acid.

As selenic acid does not react with sodium thiosulphate, it is first reduced by boiling with hydrochloric acid and titrated as above. It was found necessary to modify the method of Gooch and Evans (*Am. J. Sci.*, l., 400) for the reduction by hydrochloric acid, as there was invariably loss of selenium.

To a measured portion of selenic acid is added 25 c.c. concentrated hydrochloric acid, and the solution diluted to 100 c.c. The solution is boiled for one hour, precaution being taken not to allow the volume to go below 75 c.c., cooled, diluted with ice-water, and the selenious acid determined by titration. The following results were obtained consecutively :—

| $SeO_3$ taken. | $SeO_3$ found. | $SeO_3$ taken. | $SeO_3$ found. |
|---|---|---|---|
| 0·1011 | 0·1009 | 0·1598 | 0·1595 |
| 0·1011 | 0·1008 | 0·1598 | 0·1595 |
| 0·1067 | 0·1067 | 0·2023 | 0·2024 |
| 0·1067 | 0·1065 | 0·2665 | 0·2662 |

## Determination of a Mixture of Selenious and Selenic Acids.

Two portions of a solution containing a known quantity of selenious and selenic acids were measured off. In one the selenious acid was determined by direct titration; in the other the total selenium, after reduction of the selenic acid, was determined. On heating the solution in the reduction of selenic acid, some selenium is precipitated, which goes into solution when the chlorine is evolved. The method was tested by the following determinations :—

| $SeO_2$ taken. | $SeO_2$ found. | $SeO_3$ taken. | $SeO_3$ found. |
|---|---|---|---|
| 0·0467 | 0·0467 | 0·1013 | 0·1015 |
| 0·0467 | 0·0466 | 0·1013 | 0·1016 |
| 0·0934 | 0·0933 | 0·0506 | 0·0504 |
| 0·1868 | 0·1865 | 0·1012 | 0·1015 |

—*American Chemical Journal*, xviii., No.8.

Directorship of the Observatory of Paris.—At a recent meeting of the Academie des Sciences M. Loewy was recommended to the Minister of Public Instruction for this appointment.

* Contributions from the Chemical Laboratory of Massachusetts Institute of Technology.

# THE NEUTRALITY OF SALTS AND COLOURED INDICATORS.

## By H. LESCŒUR.

CHEMISTS formerly defined bases by their property of turning the syrup of violets green, of reddening turmeric paper, and of turning red litmus to a blue; whilst acids were characterised by their property of reddening blue litmus. On mixing acids and bases so as to neutralise their action on the coloured indicators, they obtained the *mon* or *neutral* salts—combinations of acid and of base which can neither redden blue litmus nor turn red litmus blue,—and this definition has continued to the present day.

This manner of defining the neutrality of salts has given rise to objections. Certain salts, *e.g.*, zinc sulphate, redden litmus. They are therefore not neutral according to the definition, whilst their analogies do not allow us to separate them from the salts which are truly neutral, *e.g.*, sodium sulphate. Berzelius therefore proposed, whilst retaining for the salts of potassium and sodium the signs of neutrality afforded by coloured indicators, to take no account of this character for the other metallic salts, and to agree for the nomenclature to be guided by the analogy of the corresponding sodium salts. Thus the neutral sulphates will be those which, like neutral sodium sulphate, contain three times more oxygen in the acid than in the base.

In reality at the root of this question there lies a misunderstanding on the interpretation of the indications given by litmus—a misunderstanding which prevails to this day.

Litmus contains a red colouring-matter, which forms blue compounds with alkalis. In pure water or in presence of an acid this indicator will be red. It will be blue in presence of a free alkali. In presence of an insoluble base it sometimes remains red without modification, as in the case of alumina; sometimes it gives violet compounds, insoluble or slightly soluble, more or less decomposable by water, and the solution will be more or less completely decolourised whilst ordinarily remaining rose.

If, into a solution containing an insoluble base and a mineral acid in excess, we pour an alkali in presence of litmus so as to change the medium from acidity to alkalinity, the litmus varies from red to blue, and this change is sometimes sufficiently distinct to afford a means of determination, as is the case with the salts of aluminium. But the change ensues not at the moment when the acid is saturated, and the precipitation of the acid commences, but when the precipitation is completed, and the medium contains alkali in excess.

For most of the metals the change is most obscure, and between the moment where there is still free acid and when the alkali is in excess, *i.e.*, during the period of precipitation, the litmus passes through all the intermediate shades between red and blue.

It is rational to regard as neutral the state of the medium during the course of precipitation. It then contains neither free acid nor free alkali. The case of alum and the analogous salts seems to show that the red colouration of litmus does not necessarily indicate the acidity of the medium. It may just as well signify neutrality. The different phenomena presented by other metallic salts as regards their variations and their obscurity cannot prevail against this opinion.

This interpretation is confirmed by the study of the other indicators, which are now very numerous.

Phenolphthalein is a colourless substance yielding red compounds with the alkalies. It does not combine with the insoluble metallic oxides. If into a medium containing an insoluble base, and an acid in excess, we pour an alkali in presence of phtaleine the solution will be at first colourless owing to the presence of free acid; when this is neutralised, and oxide is precipitating, it still remains colourless, and the change to redness does not take place until all the oxide being thrown down the medium contains alkali in excess.

Phthaleine by its change of colour indicates not the passage from acidity to alkalinity, but the passage from neutrality to alkalinity. Its indications are comparable to those of litmus, but are infinitely more decided.

Helianthine (Poirrier's orange No. 3) is a substance sensibly colourless in an alkaline or neutral medium, but turning red in presence of free acids. If into the solution of a metallic oxide in excess of acid we pour an alkali in presence of helianthine, the medium takes at first a rose colour; then the change to yellow takes place when all the free acid is saturated. The precipitation takes place only then. This indicator signifies therefore the passage from acidity to neutrality. The data which it yields are absolutely opposite to those of litmus and phthaleine.

*Conclusion.* — If we combine the data of these two orders of colouring matters the notion of neutrality takes a character of great distinctness. The red colouration of phthaleine, or the blueness of litmus indicating the presence of free alkali, and the rose colouration of helianthine indicating the presence of a free acid, we shall reserve the term *neutral*, for the state of a medium such that on the one part helianthine remains colourless, and on the other part phthaleine remains colourless and litmus red.

We thus recognise that salts such as alum, zinc sulphate, &c., which Berzelius considered acid to litmus, are in reality neutral to coloured reagents, and that in the question of the neutrality of salts there is agreement between theory and the data of coloured indicators.— *Comptes Rendus*, cxxiii., p. 811.

# COLOUR PHOTOGRAPHY.*

By Professor G. LIPPMANN, Membre de l'Institut (France),

(Concluded from p. 276).

How are we now to prove that the above theory is really applicable to the colour photograph you have seen? How can we demonstrate that those bright colours are due not to pigments, but to the interference, as in the case of soap-bubbles? We have several ways of proving it.

First of all, we are not bound to the use of a peculiar chemical substance, such as Becquerel's subchloride of silver; we obtain colour with a variety of chemicals. We can, for instance, dispense entirely with the use of a silver salt; a film of gelatin or coagulated albumen impregnated with bichromate of potash, then washed with pure water after exposure, gives a very brilliant image of the spectrum.

Secondly, the colours on the plate are visible only in the direction of specular reflection. The position of the source by which we illumine the photograph being given, we have to put the eye in a corresponding position, so as to catch the regularly reflected rays. In every other position we see nothing but a colourless negative. Now, as you are aware, the colours of pigments are seen in any direction. By projecting again a photograph of the spectrum, and turning it to and fro, I can show you that the colours are visible only in one direction.

Thirdly, if we change the incidence of the illuminating rays,—that is, if we look at the plate first in a normal direction, then more and more slantingly.—we find that the colours change with the incidence exactly as they do in the case of soap-bubbles or of Newton's rings; they change according to the same law and for the same reasons. The red end of the spectrum turns successively to orange, yellow, green, blue, and violet. The whole system of colours, the image of the spectrum, is seen to move down into the part impressed by the infra-red.

This is what we expect to happen with interference colours, and what again we cannot obtain with pigments.

Fourthly, if while looking at the film normally, we suffer it to absorb moisture,—this can be done by breathing repeatedly on its surface,—we see that the colours again change, but in an order opposite to that above described. Here the blue end of the spectrum is seen to turn gradually green, yellow, orange, red, and finally infra-red— that is, invisible. The spectrum this time seems to move up into the ultra-violet part of the improved film. By suffering the water to evaporate, the whole image moves back into its proper place. This experiment may be repeated any number of times.

The same phenomenon may be obtained with Newton's apparatus, by slowly lifting the lens out of contact with the plane surface. The explanation is the same in both cases. The gelatin swells up when imbibing moisture. If we consider, for instance, the violet of the spectrum, the small intervals between the strata corresponding to violet rays, gradually swell up to the values proper for green, and for red, and for infra-red; green, then red, then infra-red, are therefore successively reflected.

We will wet this photograph of the spectrum with water, project it on the screen, and watch the colours coming back in the order prescribed by theory.

It is necessary to use a transparent film, since an opaque one, such as is commonly in use, would hide the mirror from view; the sensitive substance must be grainless, or at least the grains must be much finer than the dimensions of the strata they are intended to form, and therefore wholly invisible. The preparation of transparent layers gave me at first much trouble; I despaired for years to find a proper method for making them. The method, however, is simply thus:—If the sensitive substance (the silver bromide, for instance) be formed in presence of a sufficient quantity of organic matter, such as albumen, gelatin, or collodion, it does not appear as a precipitate; it remains invisible; it *is* formed, but seems to remain dissolved in the organic substratum. If, for instance, we prepare a film of albumeno-iodide in the usual way, only taking care to lessen the proportions of iodide to ½ per cent of the albumen, we get a pefectly transparent plate, adapted to colour photography.

We want now to go a step further. It is very well for physicists to be contented with working on the spectrum, since that contains the elements of every compound colour; but we all desire to be able to photograph other objects than the spectrum—common objects with the most compound colours. We have again but to take theory as a guide, and that tells us that the same process is able to give us either simple or compound colours. We have then to take a transparent and correctly isochromatised film, exposing it with its mercury backing, then develop and fix it in the usual way; the plate, after drying, gives a correct coloured image of the objects placed before the camera. Only one exposure, only one operation is necessary for getting an image with every colour complete.

A plausible objection was offered at first to the possibility of photographing a mixture of simple colours. The objection was this: a ray of violet gives rise to a set of strata separated by a given interval; red light produces another set of strata with another interval; if both co-exist, the strata formed by the red are sure to block out here and there the intervals left between the strata formed by the violet. Is it not to be feared that one fabric will be blurred out by the other, and the whole effect marred? The confusion would be still worse if we consider the action of white light, which contains an infinity of simple components; every interval here is sure to be blocked up.

Mathematical analysis, however, shows this objection to be unfounded; we have great complexity, but not confusion. Every compound ray, both coloured and white, is faithfully rendered. As an experimental proof of this, we will project on the screen photographs of very different objects, namely, stained glass windows, landscapes from Nature, a portrait made from life, and vases and flowers.

That the colours here observed are due to interference, and not to the presence of pigments, can be shown in the same way as with the spectrum. Here, again, we observe that the colours are visible only in the direction of specular reflection, that they change with the angle of incidence, that they change and disappear by wetting, and re-appear by drying. Pigments remain equally visible and unaltered in colour under every incidence. If we attempted to touch up one of our photographs with oil or water-colours, the adulterated place would stand out on a colourless background by merely observing by diffused light. It is therefore impossible either to imitate or touch up a colour photograph made by the above-described interferential method.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.
*Ordinary Meeting, November 5th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 280).

142. "*Sulphocamphylic Acid* ($C_9H_{14}SO_5$), *with Remarks on the Constitution of Camphoric Acid and of Camphoronic Acid.*" By WILLIAM HENRY PERKIN, jun.

In two previous notices (*Proc.*, 1893, 109; 1895, 23), the author stated that when sulphocamphylic acid is fused with potash, the principal products of the reaction are two isomeric acids, $C_9H_{12}O_2$ (or $C_8H_{11} \cdot COOH$), for which he proposes the names α-*camphylic acid* and β-*camphylic acid*; the former melts at 148°, the latter at about 105°.

Besides these two acids, it has since been found that αα *dimethylsuccinic acid*, $COOH \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$, and small quantities of *dicamphylic acid*, $C_{16}H_{22}(COOH)_2$ (m. p. 225°) are formed during the fusion. The latter acid, which has not been very fully investigated, is decomposed on distillation, with formation of α-camphylic acid.

α-*Camphylic acid* (m. p. 148°) is readily acted on by phosphorus trichloride, with formation of α-*camphylic chloride*, $C_8H_{11}COCl$ (b. p. about 138—140° at 60 m.m., with decomposition). The *anilide*, $C_8H_{11}CONHC_6H_5$, melts at 111°, and the ethylic salt, $C_8H_{11}COOC_2H_5$, is a colourless oil, which distils at 132° (70 m.m.).

All these derivatives yield α-camphylic acid again on hydrolysis, and not an isomeric acid (see below under β-camphylic acid).

α-*Camphylic acid dibromide*, $C_8H_{11}Br_2 \cdot COOH$, is formed when bromine is added to the solution of α-camphylic acid in chloroform; it melts at 157°, and when digested with glacial acetic acid it is converted into *bromo-α-camphylic acid*, $C_8H_{10}Br \cdot COOH$ (m. p. 107°), with elimination of hydrogen bromide.

α-*Camphylic acid dihydrobromide*, $C_8H_{13}Br_2 \cdot COOH$, is produced by dissolving α-camphylic acid in a saturated solution of hydrogen bromide in glacial acetic acid. It melts at 156—157°, and when boiled with water or digested with quinoline it is re-converted into α-camphylic acid.

On reduction with sodium amalgam, α-camphylic acid yields *dihydro-α-camphylic acid*, $C_8H_{13} \cdot COOH$, a colourless oil, which distils at 165—170° (50 m.m.); it is an unsaturated acid, and possibly identical with the dihydro-acid obtained from β-camphylic acid by reduction (see below). When oxidised with potassium permanganate α-camphylic acid is converted into a new monobasic acid of the formula $C_8H_{13}O_3 \cdot COOH$ (m. p. 148°), and this acid, on oxidation with chromic acid, is decomposed, with formation of acetone, acetic acid, and other products which are at present under investigation.

$\beta$-*Camphylic acid*, $C_8H_{11} \cdot COOH$ (m. p. 105°), combines readily with bromine yielding $\beta$-*camphylic acid dibromide*, $C_8H_{11}Br_2COOH$ (m. p. about 177°), and this acid, when heated with glacial acetic acid, loses 1 mol. of hydrogen bromide with formation of *bromo-$\beta$-camphylic acid*, $C_8H_{10}Br \cdot COOH$ (m. p. 150°), in which the bromine atom is so firmly bound that the acid may be boiled with strong potash, or with zinc dust and acetic acid, for some time without decomposition. When digested with quinoline, there is no elimination of hydrogen bromide, but the acid is converted into $C_8H_{10}Br \cdot COOH$, *isobromo-$\beta$-camphylic acid* (m. p. 168°); probably these two bromo-$\beta$-camphylic acids are stereoisomeric.

$\beta$-*Camphylic acid hydrobromide*, $C_8H_{12}Br \cdot COOH$, is produced when $\beta$-camphylic acid is dissolved in a fuming solution of hydrogen bromide in glacial acetic acid. It melts at 138—140°, and, when boiled with water or digested with quinoline, is re-converted into $\beta$-camphylic acid.

When treated with sodium amalgam, $\beta$-camphylic acid yields an oily reduction product, $C_8H_{13} \cdot COOH$, which boils constantly at 190° (80 m.m.); this oil is probably a mixture of isomeric *dihydro camphylic acids*, as, under certain conditions, it deposits crystals of a dihydro-camphylic acid which melts at 130°.

*Iso-$\beta$-camphylic acid*, $C_8H_{11}COOH$, is formed when $\beta$-camphylic acid is digested with phosphorous tri-chloride and the product, after fractionation, decomposed with water. It melts at 130°, and is probably stereoisomeric with $\beta$-camphylic acid; the *chloride*, $C_8H_{11}COCl$, distils with very little decomposition at 135° (60 m.m.); the *ethylic salt*, $C_8H_{11}COOC_2H_5$, is a colourless oil which boils at 140° (60 m.m.), and the *anilide*, $C_8H_{11}CONHC_6H_5$, crystallises in colourless needles and melts at 103°.

When oxidised, first with potassium permanganate and then with chromic acid, $\beta$-camphylic acid yields $\alpha\alpha$-*dimethylsuccinic acid*, $COOH \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$ (m. p. 140°), $\alpha\alpha$-*dimethylglutaric acid*,—

$$COOH \cdot C(CH_3)_2 \cdot CH_2 \cdot CH_2 \cdot COOH,$$
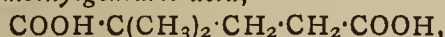
and a *ketonic acid*, $C_8H_{11}O_3$, which melts at about 50—51°.

This latter acid gives a beautifully crystalline *semicarbazone*, $C_9H_{17}N_3O_3$ (m. p. 187°); on oxidation with nitric acid, it yields $\alpha\alpha$-dimethylsuccinic acid, and, when treated with bromine and potash, it is decomposed, with formation of tetrabromomethane and $\alpha\alpha$-dimethylglutaric acid; it is therefore exceedingly probable that it is of the formula $CH_3 \cdot CO \cdot C(CH_3)_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, an *acetyl-dimethylbutyric acid*, and very likely identical with an acid, $C_9N_{11}O_3$, which Tiemann (*Ber.*, 1895, xxviii., 2176) obtained by the oxidation of $\beta$-*dihydroxydihydrocampholenic acid* with chromic acid, and to which he assigns the constitution given above.

The various decompositions of $\alpha$- and $\beta$-camphylic acids, briefly stated above, as well as the results of a number of further experiments, which the author hopes soon to be able to communicate to the Society, throw much light on the constitution of these acids, as well as on the constitution of sulphocamphylic acid, and indirectly on that of camphoric acid. In this short abstract it is, of course, not possible to enter into this matter in detail, but it may be stated that it is exceedingly difficult to account for the observed behaviour of these substances on the assumption that the formulæ either of Bredt or of Tiemann for camphoric acid are correct. If, however, camphoric acid has the constitution represented by either of the following formulæ:—

$$\begin{array}{cc}
C & CH_2 \\
(CH_3)_2C \quad CH_2 & (CH_3)_2C \quad CH \cdot COOH \\
COOH \cdot C(CH_3) \cdot CH \cdot COOH & COOH \cdot C(CH_3) \cdot CH_2 \\
I. & II.
\end{array}$$
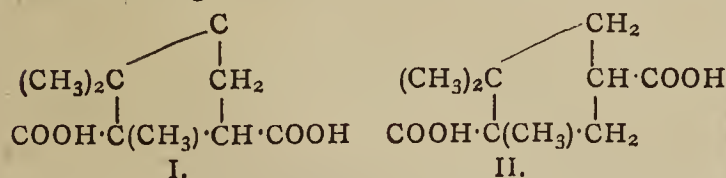
(of which the author considers formula I. the more probable), then not only the formation of acetyldimethylbutyric acid from sulphocamphylic acid, but also the various decompositions of the camphylic acids, may be readily understood, and the author has further satisfied himself that all the other reactions of camphoric acid are at least as readily, and, in most cases much more easily, explained with the help of these formulæ than with that of any other formulæ which have, so far, been suggested. The author hopes that the discussion of these new formulæ will be reserved until he has been able to explain their application in the detailed description of the experimental results indicated above.

*Camphoronic Acid.*—Bredt has assigned to this acid the formula $COOH \cdot CH_2 \cdot C(CH_3)_2(COOH) \cdot CH_2 \cdot COOH$, and it seems very probable that this expression (which also follows from the formulæ I. and II. given above) is the correct one.

Tiemann (*Ber.*, 1895, xxviii., 1089), on the other hand, represents camphoronic acid as—

$$COOH \cdot CH(CH_3) \cdot C(CH_3)_2 \cdot CH(COOH)_2,$$
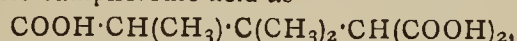
and when the paper putting forward this view appeared, the author privately suggested to Professor Tiemann that this expression could hardly be correct, since the acid, on heating, does not lose carbon dioxide, forming a corresponding dibasic acid, as would be the case if, as represented, the acid were a derivative of malonic acid.

Tiemann (*Ber.*, 1895, xxviii., 2163) replied to this that the acid did not decompose in this way, because it first loses water, and yields *anhydrocamphoronic acid*,—

$$\begin{array}{c}
CH(CH_3) \cdot C(CH_3)_2 \cdot CH \cdot COOH \\
| \qquad\qquad | \\
CO \text{------} O \text{------} CO
\end{array},$$
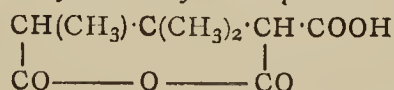
which he considers would be stable at high temperatures. But an acid of this formula is similarly constituted to—

$$\begin{array}{c}
CH_2 \cdot CH_2 \cdot CH \cdot COOH \\
| \qquad\qquad | \\
O \text{------} CO
\end{array},$$
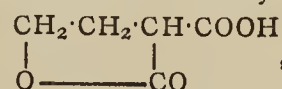
carbobutyrolactonic acid, which, at 120°, very readily decomposes, with elimination of carbon dioxide and formation of butyrolactone.

In contact with water, anhydrocamphoronic acid is at once converted into camphoronic acid, and it appeared to the author that the validity of Tiemann's formula might be tested by heating an aqueous solution of camphoronic acid at high temperatures. The result of experiments on this point showed that camphoronic acid is not appreciably decomposed when heated with water in sealed tubes at 225—235° for two hours, a result which appears to the author to prove conclusively that Tiemann's formula cannot be correct.

In confirmation of this it may be mentioned that Bredt (*Annalen*, ccxcii., 131) has lately shown that the triethylic salt of camphoronic acid, which according to Tiemann should contain the group $-CH(COOC_2H_5)_2$, does not react with sodium.

143. "*On Pettenkofer's Method for Determining Carbonic Anhydride in Air.*" By Professor LETTS, D.Sc., Ph.D., and R. F. BLAKE, F.I.C.

The authors discuss the errors in the process of absorbing the carbonic anhydride from a sample of air collected in a glass vessel by baryta, and titrating with acid, and show that, in addition to the more obvious sources of error, the action of the alkaline absorbent on the glass is one of importance.

In order to avoid it they coat both the receiver containing the air sample and the bottle holding the stock of the standard solution of baryta with paraffin wax. By this means they at once obtained more concordant results in a series of determinations. They then proceeded to test the degree, both of accuracy and of delicacy, of Pettenkofer's process if carried out with all the available precautions which suggested themselves. For this purpose they employed paraffined receiving vessels, an

apparatus for performing the titrations in a vacuum, and burettes of special construction. In addition, an apparatus was used for delivering, very accurately, measured volumes of pure carbonic anhydride into known volumes of air previously freed from that gas.

Experimenting with such mixtures of the two as occur in air, containing about 3 vols. carbonic anhydride in 10,000, the authors show that with careful work the mean error in the determinations need not exceed −0·04 part. The actual quantity of carbonic anhydride added to each receiver full of air, in a series of five experiments, amounted to 0·927 c.c.; the mean amount, found to be 0·916 c.c., giving, therefore, a mean error of −0·011 c.c.

They thus show that Pettenkofer's process, if suitably performed, is one of great accuracy and delicacy.

After giving the results of a series of determinations of carbonic anhydride in ordinary air, the authors comment on the method described by Messrs. Symons and Stephens (*Trans.*, 1896, 869) for such determinations and some of the results obtained by them. Sources of error in the process are pointed out, especially the introduction of small quantities of carbonic anhydride with the steam used to render the receiving vessels vacuous. In support of this contention they draw attention to the experiment described by Messrs. Symons and Stephens in which 0·2 c.c. of carbonic anhydride were thus found in a flask of 3 litres capacity, an amount corresponding with nearly 0·67 volumes in 10,000 supposing the flask to have been filled with air, which is nearly one-fifth the total quantity usually found in " fresh " air.

Although aware of the error thus introduced, Messrs. Symons and Stephens do not (as far as the authors can judge from their paper) make any correction for it in their subsequent determinations.

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*Ordinary Meeting, November 19th, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

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Mr. W. H. MERRETT was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. William Ross Innes, B.Sc., Ph.D., Mason College, Birmingham; Theophilus Henry Lee, Hampden House, Phœnix Street, N.W.; Frank Southerden, 75, Barry Road, Dulwich, S.E.; Basil William Turner, Collins Street, Annandale, Sydney, N.S.W.

The certificates of the following Candidates, recommended by the Council under By-law I., par. 3, were also read :—

Gopal Chandra Bauerfee, Cawnpore, N.W.P.; Eric David Ewan, Port of Spain, Trinidad.

Of the following papers those marked * were read :—

*144. " *Sulphocamphoric Acid and Derivatives of Camphorsulphonic Acid.*" By ARTHUR LAPWORTH, D.Sc., and FREDERIC STANLEY KIPPING, Ph.D., D.Sc.

The compounds obtained by treating a-bromocamphorsulphonic acid with nitric acid and with potassium permanganate respectively under various conditions, have been examined, and are described in this paper. The action of nitric acid, as stated in an earlier note (*Proc.*, 1896, xii., 77), gives rise to the formation of a *hydroxydibromocamphorsulphonic acid* of the composition $C_{10}H_{14}Br_2SO_5$, a *sulpholactone* of the composition $C_{10}H_{12}Br_2SO_4$, and a substance which was thought to be sulphocamphoric acid, but which was isolated only in the form of its ammonium dihydrogen salt.

An ammoniacal solution of potassium permanganate was found to be much more suitable than nitric acid for the oxidation of a-bromocamphorsulphonic acid, and with this reagent the principal product is sulphocamphoric acid, a simple substitution derivative of ordinary *d*-camphoric acid.

*Sulphocamphoric acid*, $SO_3H \cdot C_8H_{13}(COOH)_2$, crystallises from aqueous solution in large striated plates, which contain water of crystallisation, and from ethylic acetate in beautiful, transparent, pyramidal crystals which effloresce on exposure to the air; the anhydrous acid melts at 188°, at which temperature it is probably converted into its anhydride. It is very readily soluble in water, alcohol, acetic acid, and acetone, and has all the ordinary properties of sulphonic acids; several of its salts are described.

*Sulphocamphoric anhydride*, obtained by heating the acid with acetic anhydride, crystallises from ethylic acetate in long, colourless needles, melts at 220—222°, and is nearly insoluble in benzene and chloroform.

$SO_2Br \cdot C_8H_{13} <^{CO}_{CO}> O$, the *sulphonic bromide* of camphoric anhydride, is formed when sulphocamphoric acid is triturated with phosphorus pentabromide. It crystallises from ethylic acetate in minute pyramidal crystals, melting at 169—171°, and is not appreciably soluble in chloroform or benzene, but dissolves to a slight extent in hot carbon tetrachloride, carbon bisulphide, and xylene. When heated at its melting-point, the sulphonic bromide decomposes into sulphur dioxide and a compound which was proved to be identical with π-bromocamphoric anhydride; this fact shows that sulphocamphoric acid is derived from *d*-camphoric acid by the substitution of the sulphonic group for one atom of hydrogen.

$SO_2Cl \cdot C_8H_{13} <^{CO}_{CO}> O$, the *sulphonic chloride* of camphoric anhydride, prepared by treating sulphocamphoric acid with phosphorus pentachloride, crystallises from ethylic acetate in octahedra, needles, or prisms, according to the conditions, and melts and decomposes at 184°; it resembles the corresponding sulphonic bromide in ordinary properties, and when heated at its melting point it is converted into π-chlorocamphoric anhydride with evolution of sulphur dioxide.

*π-Chlorocamphoric acid*, $C_{10}H_{13}Cl(COOH)_2$, is obtained by dissolving the crude anhydride in concentrated nitric acid, and then evaporating the solution; it forms beautiful, transparent, apparently orthorhombic crystals, and has no definite melting point, liquefying gradually from about 195—213° according to the conditions. This compound is doubtless a derivative of *d*-camphoric acid, and is therefore an optical isomeride of the π-chlorocamphoric acid which is produced by the oxidation of optically inactive π-chlorocamphor.

*π-Chlorocamphoric anhydride* separates from a mixture of chloroform and ether in large, transparent prisms, melts at 196—197°, and resembles π-bromocamphoric anhydride in its general behaviour.

*145. " *A Compound of Camphoric Acid and Acetone.*" By WILLIAM JACKSON POPE.

Detrocamphoric acid crystallises from acetone in large, transparent tablets which belong to the orthorhombic system, and show the forms $\{100\}$, $\{010\}$, $\{110\}$, $\{120\}$, and $\{011\}$; $0.8586 : 1 : 1.2386 = a : b : c$. Although the substance is optically active in solution, no indication of hemihedral structure could be observed. The crystals have the composition $C_{10}H_{16}O_4, \frac{1}{2}Me_2CO$, and in warm weather effloresce slowly, losing their acetone of crystallisation.

These crystals seem to bear no morphotropic relationship to the ordinary monoclinic crystals of camphoric acid, but are closely related to the orthorhombic crystals of camphoric anhydride. If the forms observed on the latter be described as $\{010\}$, $\{001\}$, $\{011\}$, $\{012\}$ and $\{101\}$, the axial ratios become—

$$a : b : c = 1.0027 : 1 : 1.7216 ;$$

similarly the indices of the forms observed on the compounds of camphoric acid and acetone may be described as $\{010\}$, $\{001\}$, $\{011\}$, $\{012\}$, and 110, whilst the axial ratios simultaneously change to—

$$a : b : c = 1.2386 : 1 : 1.7172.$$

It thus becomes evident that of the five forms present on each set of crystals, four lying in one zone, namely, $\{010\}$, $\{001\}$, $\{011\}$, and $\{012\}$, have the same indices on both; the further remarkable result is obtained that any angle in this zone on crystals of the one substance is practically equal to the corresponding angle in the same zone on the other set of crystals.

*146. "*Mercury Hyponitrites.*" By P. C. RAY, D.Sc.

By the dissociation of mercurous nitrite a neutral solution is obtained containing both mercurous and mercuric nitrites. When this solution is mixed with a dilute solution of sodium hyponitrite, both mercurous and mercuric hyponitrites are apparently formed.

Mercurous nitrate, when similarly treated, does not yield a hyponitrite.

*147. "*The Nitrites of Mercury and the Conditions under which they are Formed.*" By P. C. RAY, D.Sc.

The author finds (1) that mercurous nitrite is always formed by the action of dilute nitric acid (10 to 23 per cent) on mercury at a temperature of about 32°. (2) That the mercurous nitrite thus formed slowly dissolves in the mother liquor, resulting in the production of mercurous nitrate of two kinds:—(a) Monohydrated mercurous nitrate, $Hg_2(NO_3)_2 + 2H_2O$; and (b) the basic nitrate, named "Marignac's salt." (3) That when a neutral dilute solution of mercurous and mercuric nitrites (the products of dissociation) is allowed to evaporate spontaneously, monohydrated mercurous nitrite, $Hg_2(NO_2)_2 + H_2O$, and two basic mercuroso-mercuric nitrites and a basic mercuric nitrite are successively formed. (4) That of these salts only two may be said to contain real "water of crystallisation," namely, those termed monohydrated mercurous nitrite and nitrate respectively, in that they are efflorescent, losing water rapidly in a dry atmosphere. The others apparently contain "water of constitution."

*148. *The Interaction of Mercurous Nitrite and the Alkyl Iodides.*" By P. C. RAY, D.Sc.

By the interaction of ethyl iodide and mercurous nitrite the author has apparently obtained ethyl nitrite and nitro-ethane.

149. "*Crystallography of the Monohydrated Mercurous Nitrite.*" By T. H. HOLLAND, F.G.S.

The crystals belong to the triclinic system, and exhibit strong double refraction. Macropinacoidal sections show an extinction angle of 33° to the vertical crystallographic axis.

*150. "*On the Identity of Dextrose from Different Sources; With Special Reference to the Cupric Oxide Reducing Power.*" By C. O'SULLIVAN, F.R.S., and A. L. STERN, D.Sc.

Dextrose was prepared from sugar (cane and beet), starch, and lactose, and the optical activity, the cupric oxide reducing power, and the specific gravity of the aqueous solutions of each specimen determined. These factors were found to be the same for each of the different specimens of dextrose, and consequently from this evidence it is concluded that the dextroses from various sources are identical.

The figures obtained for the cupric oxide reducing power are practically the same as Allihn's, which are in common use in Germany, although the former were obtained by proceeding according to the directions previously given by O'Sullivan, which, however, do not differ materially from Allihn's. A modified form of filtering tube is described, which was found to possess several advantages.

151. "*Note on Mr. W. J. Humphreys' Paper on the Solution and Diffusion of certain Metals in Mercury.*" By Prof. ROBERTS-AUSTEN, C.B., F.R.S.

In the April number of the *Transactions* (lxix., 243) there is an interesting communication on the above subject by Mr. Humphreys, who is the first to publish results in continuation of Guthrie's experiments (1883) on diffusion in mercury, and his work is, therefore, very welcome. As, however, I have, at intervals since 1882, conducted experiments on the diffusion of molten metals (Bakerian Lecture, *Phil. Trans.*, 1896, clxxxvii.), I would briefly refer to certain portions of Mr. Humphreys' work that are difficult to interpret by calculation, and I may offer a few suggestions in the hope that they will be useful in future work.

Mr. Humphreys has not attempted to calculate absolute *diffusivities* from the results of his well-devised experiments. It is, in fact, very difficult to do so, on account of his having used a solid metal instead of a dilute amalgam, from which diffusion into mercury took place. Guthrie did the same, and this precludes the possibility of using the results of either experimenter for calculating absolute diffusivities by the direct application of Stefan's tables (Stefan, *Wien. Akad. Ber.*, 1879, lxxix., 161; see also Roberts-Austen, *loc. cit.*).

Approximate results by calculation appear to show, however, that there is a general concordance between the results of Guthrie and of Humphreys; but more satisfactory results would be afforded if Mr. Humphreys arranged his experiments with a view to their final calculations by means of Stefan's tables.

It is hardly necessary to say that the use of a solid metal diffusing into a fluid one—solid silver into mercury for instance—would introduce the complications arising from the fact that amalgamation or solution of the solid metal must necessarily precede diffusion, and it is very difficult to fix the degree of concentration of the dissolved metal in the layer of amalgam so formed, from which diffusion actually takes place.

Mr. Humphreys states that the rate of diffusion of silver and copper into mercury is 600 times as rapid as that of zinc into mercury, and he expressed a doubt whether this might not be due to superior density of silver amalgam as compared with mercury. Some forty-six years ago, Joule ("Collected Papers," i., 460), working on amalgams of silver and of copper, gave evidence which points to the conclusion that dilute amalgams of these metals would prove to be denser than mercury itself. Mr. Humphreys used single tubes filled with mercury, and silver and copper were respectively placed at the top of fluid columns. The diffusion of silver must be studied by the use of dilute amalgams diffusing upwards, and if, for the purpose of demonstration, Mr. Humphreys will employ U-tubes, as Mr. Stansfield has recently in my laboratory, he will find the amalgamated silver falls rapidly down one limb by density, and slowly rises by diffusion through the mercury in the opposite limb, the diffusitivity of silver being, in fact, of the same order as that of zinc which Mr. Humphreys considered to diffuse so slowly.

152. "*Solution and Diffusion of certain Metals and Alloys in Mercury.* Part II." By W. J. HUMPHREYS.

The author has extended this investigation (*Proc.*, 1896, xii., 9) to aluminium, antimony, cadmium, magnesium, thallium, and a few alloys. Aluminium and antimony diffuse in mere traces. The cadmium amalgam heavier than mercury was not formed. The author considers that solution and diffusion in mercury may serve to distinguish between mixtures and compounds in the case of alloys. Metals that belong to the same group in Mendeleeff's table increase in their power of solution and diffusion with their atomic weight.

153. "*Note on the Heat of Formation of the Silver Amalgam,* $Ag_2Hg_8$." By FANNIE T. LITTLETON.

In a previous communication (*Trans.*, 1895, lxvii., 239) an account was given of a silver amalgam exhibiting remarkable behaviour on being moderately heated, swelling up as if from the evolution of gas, and becoming hard, brittle, and crystalline in structure. It was noted that this behaviour was most marked when the silver and mercury were present in the ratio of 1 atom of the former to 4 of the latter, and that, when these metals were

brought together, the silver in the state of a fine crystal-line powder (as reduced from the pulverulent chloride by zinc and a little hydrochloric acid), and the mercury simply poured over it, there was very considerable rise of temperature, amounting to 38° or 40°, so that the amalgam could not be borne on the palm of the hand without pain.

No actual measurement of the heat evolved in the formation of the amalgam was made. Such measurements have recently been made in a simple form of calorimeter, with the following result :—

If the formula assumed for the amalgam be $Ag_2Hg_8$, and the molecular weight be taken as 1813·8 ($H = 1$), the heat evolved in the formation of 1 molecule is equal to about 3432 units, the molecular weight being counted in grms., and the unit of heat as the heat required to raise the temperature of 1 grm. of water (at about 22°) by 1°. These determinations gave the values 3395, 3418, and 3484. It is to be observed that the amalgam, just after its production, is a soft, pasty, semi-fluid mass. Calculating from Person's figures, for the latent heat of fluidity of the metals concerned, 1813·8 grms. of the amalgam consists of 215·4 grms. of silver, the fusion of which would absorb 4537 heat units and 1598·4 grms. of mercury, the solidification of which would evolve 4507 heat units.

Two nearly-agreeing determinations of the specific heat of the amalgam, in its freshly-formed condition, gave an average value of 0·029 referred to an equal weight of water as unity. This is notably below 0·0359, the result of calculation from the specific heats of the respective metals, assuming these to remain unchanged in the amalgam.

154. "*Preliminary Note on the Action of Alkyl Iodides on Silver Malate.* By THOMAS PURDIE, F.R.S., and G. DRUCE LANDER, B.Sc.

In a recent communication to the Society (Purdie and Williamson, *Trans.*, 1896, lxix., 818), on the optical activity of ethereal malates and lactates prepared by different methods, it was shown that, while the action of methylic, ethylic, *n*-propylic, and *n*-bytylic iodides on silver malate proceeded apparently in the normal manner, the action of isopropylic iodide was anomalous. The ethereal salt obtained from the latter reaction was small in quantity ; the percentages of carbon and hydrogen found on analysis were considerably higher than the numbers calculated for isopropylic malate, and the liquid showed a much higher activity than this substance should possess. The authors have repeated the experiment on a larger scale, and find that the high activity of the product is due to the presence in it of about 20 per cent of isopropylic isopropoxysuccinate. It appears that the isopropyl group of the iodide replaces not only the silver of the malate, but also, to a considerable extent, the hydrogen of its alcoholic hydroxyl.

The isopropylic isopropoxysuccinate was obtained by the partial hydrolysis of the product of the reaction, the malate being more easily hydrolysed than the other compound. The rotation of the mixture produced by the reaction was $\alpha = -32\cdot96°$ ($l = 1$), that of the isopropoxy-succinate was $-57\cdot08°$. The results of the analysis of the ethereal salt, and also of the barium, calcium, and potassium salts obtained from it, were in agreement with the calculated numbers. The specific rotations in aqueous solutions of varying concentration were determined for the acid, also for the barium, calcium, acid potassium and normal potassium salts, and were found in general to approximate to the corresponding numbers for active normal propoxysuccinic acid prepared by resolution of the inactive compound (*Trans.*, 1895, lxvii., 949).

In the paper on ethereal malates and lactates (*loc. cit.*) it was pointed out that the ethereal salts made from the silver salt possessed in every case a notably higher activity than those made by the hydrochloric and sulphuric acid methods. The obvious conclusion that the difference was due to the presence of racemoid substance in the latter compounds was negatived by experiments which failed to detect in them such a quantity of racemoid compound as would account for their lower activity. The cause of the anomaly was left unexplained. After the authors had discovered, however, that isopropoxysuccinic acid was produced in considerable quantity by the reaction of isopropylic iodide on silver malate, it seemed probable that the higher activity of the other malates, made by the same method, might also be due to their being contaminated with small quantities of the corresponding alkyloxysuccinates. In the case of ethylic malate an admixture of about 4 per cent of ethylic ethoxysuccinate would suffice to account for the higher observed activity ; its presence could not be detected by analysis, nor in the course of ordinary fractional distillation, the differences in the boiling-points of the substances being inconsiderable.

To test the correctness of the suggested explanation, the authors prepared ethylic malate from the silver salt on a large scale. The crude product boiled at 130—135° at about 15 m.m., and showed the activity $\alpha = -13\cdot93°$ ($l = 1$). On re-distillation, the activity of the first fraction collected showed a rise of about 1°, and after often-repeated fractional distillation, two fractions were finally obtained, differing in boiling-point by only about 3°, the lower boiling fraction, however, having the activity $\alpha = -17\cdot05°$ ($l = 1$) and the higher boiling $\alpha = -12\cdot26°$. By partial hydrolysis of the former fraction the activity of the unhydrolysed oil was raised to $-20°$. The rotation of ethylic malate made by the mineral acid methods was previously found to be $\alpha = 11\cdot7°$. The ethylic malate made by the silver salt method is, therefore, evidently contaminated with a small quantity of a much more active compound, and although efforts to isolate the substance in the pure state have so far been unsuccessful, it is very probable, judging from the case of isopropylic iodide, that the compound in question is ethylic ethoxysuccinate.

Experiments show that the ethereal salts of malic acid, and, no doubt, of other hydroxy-acids, cannot be obtained in the pure state from the silver salt ; by the action of isopropylic iodide, isopropylic isopropoxysuccinate is produced in quantity, and the higher activities found for other malates prepared by this method, which are quoted in the paper referred to, are due probably to the presence of small quantities of the ethereal salts of the highly active alkyloxy-acids. The high activity of the ethereal lactates made from the silver salt, which the authors are at present examining, will probably find a similar explanation.

The authors are not aware that the production of alkyloxy-acids by the action of alkyl iodides on silver salts of hydroxy-acids has ever been observed. The reaction is remarkable, and the authors are investigating it further.

155. "*On certain Thiocarbimides derived from Complex Fatty Acids.*" By AUGUSTUS E. DIXON, M.D.

In this paper an account is given of the preparation of thiocarbimides derived from palmitic and stearic acids ; the compounds in question, if brought into contact with organic bases, afford the corresponding substituted thiocarbimides, or thioureas ; from these, in turn, by suitable treatment with silver compounds, their oxygen analogues may be obtained.

*Palmitylthiocarbimide*, $C_{15}H_{31}CO \cdot NCS$, is an easily fusible, soft solid, of faintly pungent odour; it distils, with considerable decomposition, between 200° and 205°, and is attacked by water, yielding palmitic and thiocyanic acids. ab - *Palmitylphenylthiocarbamide*, $C_{15}H_{31}CO \cdot NH \cdot CS \cdot NHPh$, crystallises from alcohol in slender, waxy-looking needles, insoluble in water, soluble in the ordinary organic solvents, and melting at 62—63° (uncorr.). The corresponding *urea* forms microscopic needles ; m. p. 90—91°. ab-*Palmitylorthotolylthiocarba-*

*mide*, $C_{15}H_{31}CO \cdot NH \cdot CS \cdot NHo\text{-}To$, felted white needles, melting between $65 \cdot 5$ and $66 \cdot 5°$. The *urea* occurs in woolly masses of flexible needles; m. p. 98°. *ab-Palmitylparatolylthiocarbamide*, and *palmitylparatolylurea*, fine needles, melting at 75—76°, and 89—90° respectively. $C_{15}H_{31}CO \cdot N:C(SH) \cdot NMePh$, *n-palmityl-v-methylphenylthiourea*, white needles; m. p. 59—60°. *n-Palmityl-v-phenylbenzylthiourea*, $C_{15}H_{31}CO \cdot N:C(SH) \cdot NPhBz$, was obtained in nearly quantitative amount; it melts at 62—63°, and by desulphurisation affords the *urea*, $C_{15}H_{31}CO \cdot NH \cdot CO \cdot NPhBz$, pearly needles of m. p. 68—69°. *ab-Stearylorthotolylthiocarbamide*,—

$$C_{17}H_{35}CO \cdot NH \cdot CS \cdot NHo\text{-}To,$$

is deposited from absolute alcohol in very fine white needles, melting at 67—68°; by treatment with silver nitrate it affords *stearylorthotolylurea*, m. p. 94—95°. $C_{17}H_{35}CO \cdot NH \cdot CS \cdot NH \cdot C_6H_3Me_2$, *ab-stearylmetaxylylthiocarbamide*, lustrous needles, melting at 71—72°; the corresponding *urea* melts at 92—93°. *ab-Stearylalphanaphthylthiocarbamide*, melts at 80—81°; the *urea* at 114—115°. *n-Stearyl-v-phenylbenzylthiourea*,—

$$C_{17}H_{31}CO \cdot N:C(SH) \cdot NPhBz,$$
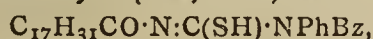
melts at 66—66·5°. and by desulphurisation affords the *urea*, $C_{17}H_{35}CO \cdot NH \cdot CO \cdot NPhBz$; the latter forms white needles, becoming electrical on friction, and melting between 74° and 75°.

It is stated by Miquel (*Ann. Chim. Phys.*, [5], xi., 316) that benzoylthiocarbimide, $PhCO \cdot NCS$, even if heated at 200° with diethylamine, remains unaltered; the author finds, however, that solutions of these two substances, in benzene and alcohol respectively, interact spontaneously, with marked evolution of heat, and production of *n-benzoyl-v-diethylthiourea*, $PhCO \cdot N:C(SH) \cdot NEt_2$. The latter forms long, brilliant prisms, sparingly soluble in boiling water; m. p. 100—101° (corr.).

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## EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

*First Ordinary Meeting, November 30th, 1896.*

Prof. A. CRUM BROWN, President, in the Chair.

THE PRESIDENT opened with his Inaugural Address, taking as his subject "*The Life and Work of Kekulé.*"

He first referred to the fact that since the last address he had given to the Society there had passed away one of the most distinguished chemists of his time.

After a short sketch of Kekulé's life, Professor Crum Brown referred to the most important of his discoveries and speculations :—The Quadrivalence of Carbon, the Constitution and Relation of Maleic, Fumaric, and Succinic Acids, and of Citraconic, Itaconic, Mesaconic, and Pyrotartaric Acids; the Constitution of Benzene and of Aromatic Compounds generally. He stated his belief that even now, after the enormous extension of aromatic chemistry due to Kekulé's ideas, Kekulé's original formula for benzene remains, on the whole, the most satisfactory.

Among the later works of Kekulé, his investigation into the so-called carboxyltartronic acid was discussed in its bearings on the constitution of benzene.

In conclusion, the President indicated to how great an extent our present ideas and our present knowledge of the facts of organic chemistry are directly due to Kekulé or to his influence, and recommended a study of his individual papers. These are not very numerous, but every one is of a classical character.

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**Distribution of Lipase in the Organism.** — M. Hanriot.—It results that the lipasic ferment is absent in most of the organs except in the pancreas and liver.— *Comptes Rendus*, cxxiii., No. 20.

## NOTICES OF BOOKS.

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*The Gases of the Atmosphere: their History and their Discovery.* By WILLIAM RAMSAY, F.R.S., Professor of Chemistry in University College, London. With Portraits. London: Macmillan and Co. (Ltd.). New York: The Macmillan Co. Pp. 240. 1896.

IN his Preface the author reminds us that the discovery of argon, in 1894, re-opens a chapter in chemistry which had been considered as closed,—that is, the composition of the atmosphere and the number and the attributes of its ingredients. The accounts of the gas as submitted to the Royal Society, by Lord Rayleigh and Prof. Ramsay, and verified by other chemists and physicists, were written in a style adapted to experts only, and the paraphrases of these first announcements which figured in popular organs were—as usual in such cases—lacking in precision. Hence the author finds it desirable to submit to the public a correct account of this discovery and of the steps by which it has been reached. In so doing he has expounded the results of earlier experiment and speculation concerning the composition of the atmosphere. In this study we are introduced to some eminent men of Science,—Boyle, Mayow, and Hales,—now most undeservedly forgotten. These investigators, we find, were all Oxford men. In those days Oxford had not lost sight of the beacon light raised by the elder Bacon, which we may hope she is beginning to again recognise. The early death of Mayow—lost to Science in his thirty-fourth year —is justly deplored. It appears not unlikely that, had he reached an average age, he would have anticipated the illustrious Lavoisier, and the world might thus have been spared the delusions of the Phlogistian School. The rise and persistence of this School was particularly unfortunate for English Science. Hales and Priestley were both experimentalists, but they derived little benefit either from their own experiments or from those of Mayow.

The next forward step in pneumatic chemistry was Black's discovery of carbon dioxide—the first ingredient of the air which was definitely recognised, and was not again lost sight of as was Mayow's "fire-air." Daniel Rutherford, a pupil of Black, is here duly credited with the discovery of nitrogen, or, as it was called, "phlogisticated air." Cavendish unfortunately did not appeal to the balance to check his results.

With the avatar of Lavoisier's new system of chemistry—"*la chimie Française*" as it was called by some —the study of the atmosphere was laid aside as complete. But in 1882 Lord Rayleigh, in his presidential address to the Physical Section of the British Association, referred to an investigation on the relative densities of hydrogen and oxygen. His object was to ascertain whether the atomic weight of these gases, as determined from their densities and combining volumes, were exactly as $1 : 16$. After prolonged experimentation he came to the conclusion that the atomic weight of oxygen must be 15·882, hydrogen being 1. The percentage of oxygen must be 20·941, and that of nitrogen 79·059, to give a mixture a litre of which weighs 1·29327 grms. For these experiments the nitrogen was prepared by several methods. It was then found that nitrogen obtained by the decomposition of ammonia was somewhat lighter than atmospheric nitrogen, the deficiency being about 1 part in 200. Further experiments showed that in every case the nitrogen, from all sources except the atmospheric, weighed rather less than atmospheric nitrogen. Lord Rayleigh now found that the atmospheric nitrogen contained a residuum of a gas which, unlike pure nitrogen, would not disappear on " sparking" with oxygen in presence of caustic soda.

By the meeting of the British Association at Oxford (August, 1895) the evidence for the presence of a new constituent gas in the atmosphere was such as to warrant its publication. It was received with interest, not un-

mixed with scepticism. One of the audience put the curious question, whether the name of this new substance had been discovered? It was found that the new substance (to which the name of argon had been ascribed, from its chemical inertness) is present only in the atmosphere, in the gases extracted from certain mineral waters, in one meteorite, and in a few more minerals. It does not appear to be present in any appreciable proportion in any animal or vegetable matter ; nor does it appear to have any action upon living organisms.

Among the mineral waters richest in argon are those of Bath and Buxton, and Allhusen's Well at Middlesborough.

Helium, which has properties rather similar to those of argon, is not found in the atmosphere.

Prof. Ramsay's work is of exceeding interest as showing the niceties demanded in such investigations. Hence it will prove a most instructive study for chemical students of all ages.

## CORRESPONDENCE.

### THE PROXIMATE CONSTITUENTS OF COAL

*To the Editor of the Chemical News.*

SIR,—The report of the B.A. Committee of investigation of the above subject, published in recent issues of the CHEMICAL NEWS (vol. lxxiv., pp. 261, 271), puts us in the unpleasant position of having to deal with a question of priority.

The only "new" matter in the report is contained in results of chlorination methods applied to the coals. The "composition and physical properties of the chlorinated compounds obtained," the report mentions incidentally, "recall those described by Messrs. Cross and Bevan in their investigations of jute."

This re-discovery of our results of fifteen years ago we note as a confirmation of ancient work : we make no protest on this ground. What we do object to is the much larger *suppressio veri.* The facts are these :—

In 1880—82 we extended the methods of enquiry which we had found useful in resolving the problem of the constitution of the ligno-celluloses specifically to the coals, regarded as extreme terms of the series of natural condensation products of the celluloses. We isolated from the coals a series of chlorinated compounds having identical features with those described in the report in question. We obtained from the celluloses, by the action of $H_2SO_4$ at 70°, products of condensation separating as gelatinous hydrates and passing by spontaneous dehydration into black lustrous solids, having all the external characteristics of the coals, from which chlorinated derivatives were obtained, one of which had the formula $C_{21}H_{16}Cl_4O_{10}$. We showed the connection of these compounds with the "humic" series of condensation products of the carbohydrate group, obtained by both natural and artificial processes, which also yield products of chlorination similar in composition and identical in characteristics (Sestini). We studied the action of nitric acid on the coals, and showed that substitution derivatives were obtained, and also we called attention to a remarkable paper of Hatchett's, published in the *Phil. Trans.* in 1805, dealing with the action of nitric acid on a wide range of "organic" compounds of this class. We also studied the action of sulphuric acid on these condensation products, and showed that its deoxidation to sulphurous acid was accounted for by a sulphonation of CH residues (as a first stage in the deoxidation), followed by oxidation of the C atoms themselves. We also proposed to designate this group of "carbonaceous" compounds by the term "pseudo-carbon," to emphasise the difference

thus revealed in their properties and reactions from those of elementary carbon in its amorphous forms.

These results are fully recorded in a series of publications, viz , *Journ. Chem. Soc.,* xli., 103 ; xliii., 21 ; *Phil. Mag.,* v., 13, 325 ; 14, 346 ; *Brit. Assoc. Report,* 1881,— of the existence of which we have reason to know the Committee was aware.

The report, upon the basis of its contribution of new matter, cannot make any claim to have advanced our knowledge of the coals beyond the point to which it was carried fifteen years ago.

Without insisting on the personal aspect of the matter, the form of the report amounts to a deliberate setting aside of scientific records, and although we have a particular objection to "priority grievances," and should never raise a question where an obvious oversight is involved, the present case leaves us no alternative but to protest.—We are, &c.,

CROSS and BEVAN.

4, New Court, Lincoln's Inn, W.C.,
    December 7, 1896.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 20, November 16, 1896.

**Researches on Phosphoric Acid. Determination of Pyrophosphoric Acid.**—M. Berthelot and G. André.

**Transformation of Pyrophosphoric Acid.** — M. Berthelot and G. André.—These two connected papers will be inserted in full.

**On the Earths of the Yttria Group contained in the Monasite Sands.** — P. Schützenberger and Boudouard.—This paper also will be inserted *in extenso.*

**Densities of Nitrogen, Oxygen, and Argon, and the Composition of Atmospheric Air.**—A. Leduc.—The discovery of argon has modified a number of the results formerly published by the author : atomic weights, molecular volumes, and especially the density of nitrogen. He had besides been led to resume the study of some gases, and particularly that of oxygen, the density of which appears slightly too low in comparison with chemical nitrogen. His new experiments show the density of nitrogen in comparison with atmospheric air as 0·96717. For the density of oxygen he admits the figure 1·10523, being convinced of the insufficiency of platinum sponge. *Argon.*—For the proportion of argon in atmospheric air he finds 0·0119, and for its density 1·376. The mean composition of atmospheric air is shown in the following table :—

| | Nitrogen. | Oxygen. | Argon. |
|---|---|---|---|
| By weight .. .. | 75·5 | 23·2 | 1·3 |
| By volume .. .. | 78·06 | 21 | 0·94 |

**Cock for Receivers destined for Compressed or Liquefied Gases.**—E. Ducretet and L. Lejeune.—The structure of this appliance cannot be shown without the accompanying figure.

**Neutrality of Salts and Coloured Indicators.**—H. Lescœur.—(See p. 285).

**Analysis of Air by Agaricus atramentarius.**—Dr. T. L. Phipson.

**Some Properties of Pure Glucina.**—P. Lebeau.—Pure glucina is fusible and volatile at the temperature of the electric furnace. It does not vary appreciably in density, and retains the property of being attackable by concentrated acids. Boron, silicon, and carbon are the

only non-metals capable of reducing glucina and yielding crystalline compounds. The reductive metals—sodium, potassium, magnesium, and aluminium, have no action.

**Action of Sulphuric Acid and Iodine upon Iodic Acid.**—Paul Chretien.—By this reaction the author obtains crystals containing when dry 99·6 per cent of iodic anhydride. He finds in 100 parts—

| | |
|---|---|
| Iodine liberated by water .. .. .. .. | 25·98 |
| Iodine remaining as iodic acid.. .. .. | 38·07 |
| Oxygen.. .. .. .. .. .. .. .. | 12·17 |
| Sulphuric anhydride .. .. .. .. .. | 20·46 |
| Water .. .. .. .. .. .. .. .. | 2·3 |
| | 99·98 |

Ratio of iodine to oxygen 5·291.

**Molybdenum Iodide.**—M. Guichard.—Molybdenum iodide, $MoI_2$, may be prepared in the amorphous state by the action of hydriodic acid upon molybdenum chloride.

**Separation of Tungsten from Titanium.**—Ed. Defacqz.—The sample, whether a mixture of the two acids, calcined, or not, or an alloy, is treated in a platinum crucible with 7 to 8 times its weight of a mixture of 8 parts potassium nitrate and 8 parts potassium carbonate. It is heated to dull redness for twenty to thirty minutes, when there is obtained a white mass, which, when cold, is taken up in water. The product is evaporated to dryness in the water-bath. It is washed at first by decantation, and the insoluble part is further washed upon the filter with water containing ammonium nitrate. In the liquid to which the washings have been added the tungsten is determined as mercurous tungstate with the usual precautions. The residue on the filter is dried and ignited, and treated with potassium bisulphate, in order to determine the titanium in the general manner.

**Spectrum of the Chlorophylls.**—A. Etard.—This paper will be inserted in full.

**Fixation of Atmospheric Nitrogen by the Association of Algæ and Bacteria.**—Raoul Bouilhac.—The author's experiments show that *Schizothrix lardacea* and *Ulothrix flaccida* cannot grow in nutrient solutions void of nitrogen, even in presence of the bacteria of the soil. It is quite otherwise with *Nostoc punctiforme*. The association of this algæ with the bacteria permits the simultaneous development of the two species and the fixation of nitrogen ensues most distinctly. Both the *nostoc* and the bacteria in question can flourish in a solution containing 1/10,000 of arsenic.

**Organic Matter in the Mineral Water of Tulba-Haut (Haute Garonne).**—F. Garrigou.—The author records the presence of an organic alkaloid as more distinct than in any other mineral water.

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*Zeitschrift für Analytische Chemie.*
Vol. xxxv., Parts 4 and 5.

**Detection of Sugar.** — Neitzel (*Deutsch. Zucker Industrie* and *Chemiker Zeitung*).—The author substitutes camphor for a-naphthol.

**Determination of Nitrogen in Organic Substances.**—C. E. Zay and Haselhoff (*Chemiker Zeitung*).—Modifications of the Kjeldahl process.

**Relations of Contraction on mixing Acetone with Water.**—K. P. McElroy.—The greatest contraction is 4 per cent.—*Journ. Am. Chem, Soc.*

**Volumetric Determination of Hydroxylamine by means of Solution of Iodine.**—Tamemasa Haga.—From the *Journal of the Chemical Society.*

**Determination of Parasulphanilic Acid.**—K. Brenzinger (*Zeit. Angewandte Chemie*).—Parasulphanilic acid, on treatment with nascent bromine or bromine-water, is converted into tribromaniline with abscission of sulphuric acid. Orthosulphanilic acid behaves in a similar manner.

The author proceeds as follows :—A quantity corresponding to about 1·73 grms. sulphanilic acid is dissolved in about 100 c.c. of water, slightly acidified, and saturated bromine water is added until a distinct reaction is obtained on potassium iodide starch-paper, like that assumed at the conclusion of a diazotation. It is allowed to stand for about thirty minutes. It is then rendered distinctly alkaline with ammonia or sodium carbonate, heated almost to ebullition, and filtered. In the filtrate the sulphuric acid formed is determined in the usual manner. The precipitation, filtration, and washing of the barium sulphate must be effected in as great a heat as possible, especially if metasulphanilic acid is the predominating ingredient.

**Determination of Value of Naphtholic and Naphthylaminic Sulpho-Acids.**— W. Vaubel (*Chem. Zeit.*).—The author has extended his process to a number of new components.

**Colorimetric Determination of Carbohydrates.**—Neitzel. — This method has been patented by the author (!)

**Determination of Cane-sugar in presence of Milk-sugar.**—W. D. Bigelow and K. P. McElroy.—From the *Journ. Am. Chem. Soc.*

**Determination of pre-existing Sugar in Green Malt.**—J. Jais.—A combination of the two methods already known.

**The Chemical Composition of Fruit-Wines and their Distinction from Grape-Wines.** — Kuhlisch (*Chemiker Zeitung*).—The alcohol per cent in ciders is low, ranging from 4·29—5·86 per cent, but the extractive and mineral matters are higher than in grape-wines. The tannin is very slightly higher than in white grape-wines, but the nitrogen is considerably lower. The only certain distinction between fruit and grape wines is that the former contain no tartaric acid nor its salts. Certain American and English ciders and perries contain much unfermented sugar (Embrey, *Analyst*). White and red currant wines prepared by the addition of sugar to the fruit juice before fermentation may contain 13 grms. alcohol in 100 c.c., and only 0·007 phosphoric acid.

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# MISCELLANEOUS.

**Society of Public Analysts.**—The following nominations have been made for Officers and Council for the year 1897.

*President*—Bernard Dyer, D.Sc.

*Vice-Presidents* (who have filled the office of President)—M. A. Adams, F.R.C.S.; A. H. Allen; Sir Charles A. Cameron, M.D., F.R.C.S.; A. Dupré, Ph.D., F.R.S.; Otto Hehner; Alfred Hill, M.D., F.R.S.E.; J. Muter, M.A., Ph.D., F.R.S.E.; Thos. Stevenson, M.D., F.R.C.P. (Who have not filled the office of President)—A.P. Aitken, D.Sc., F.R.S.E.; W. W. Fisher, M.A.; John Pattinson.

*Treasurer*—E. W. Voelcker.

*Hon. Secretaries*—E. J. Bevan; Charles E. Cassal.

*Other Members of Council* — R. Bodmer; A. Wynter Blyth, M.R.C.S.; A. C. Chapman; S. Rideal, D.Sc.; J. E. Stead; J. A. Voelcker, M.A., B.Sc., Ph.D.

The names of those Members of Council who do not retire this year are—Leonard Archbutt, Bertram Blount, E. Russell Budden, W. J. Dibdin, Sidney Harvey, and Alfred Smetham.

**Royal Institution.**—His Royal Highness the Prince of Wales has consented to open on Tuesday afternoon, December 22nd, 1896, the Davy-Faraday Research Laboratory of the Royal Institution, founded by Dr. Ludwig Mond, F.R.S., as a memorial of Davy and Faraday. The ceremony will take place in the theatre of

the Royal Institution, where, by desire of His Royal Highness, Professor Dewar will after the opening ceremony show experiments illustrative of the use of "Liquid Air in Scientific Research." The following are the lecture arrangements before Easter:—Professor Silvanus P. Thompson, six lectures (adapted to a Juvenile Auditory) on "Light, Visible and Invisible"; Professor Augustus D. Waller, twelve lectures on "Animal Electricity"; Professor Henry A. Miers, three lectures on "Some Secrets of Crystals"; Dr. J. W. Gregory, three lectures on "The Problems of Arctic Geology"; Professor Percy Gardner, three lectures on "Greek History and Extant Monuments"; Professor W. Boyd Dawkins, three lectures on "The Relation of Geology to History"; Mr. Carl Armbruster, three lectures on "Neglected Italian and French Composers"; Mr. Walter Frewen Lord, three lectures on the "Growth of the Mediterranean Route to the East"; and the Right Hon. Lord Rayleigh, six lectures on "Electricity and Electrical Vibrations." The Friday Evening Meetings will begin on January 22nd, when a discourse will be given by Professor Dewar; succeeding discourses will probably be given by The Right Rev. The Lord Bishop of London, Professor Jagadis Chunder Bose, Professor John Milne, Dr. G. Johnstone Stoney, Lieut.-Col. C. R. Conder, R.E., Mr. Shelford Bidwell, Professor Arthur Smithells, Sir Edward Maunde Thompson, Sir William Turner, Mr. Charles T. Heycock, the Right Hon. Lord Rayleigh, and other gentlemen.

## MEETINGS FOR THE WEEK.

WEDNESDAY, 16th.—Society of Arts, 8. "The Chamber Music of Purcell, Handel, and Bach," by Arnold Dolmetsch.
THURSDAY, 17th.—Chemical, 8. "Experimental Methods employed in the Examination of the Products of Starch Hydrolysis," "Specific Rotation of Maltose and of Soluble Starch," "Relation of the Specific Rotatory and Cupric Reducing Powers of Starch Hydrolysis by Diastase," by Horace T. Brown, F.R.S., G. H. Morris, Ph.D., and W. H. Millar.

# THE CHEMICAL NEWS.

## NOTE ON
## A CASE OF POISONING BY ARECA NUT.

By ERNEST H. COOK, D.Sc., (Lond.), A.R.C.S.,
Clifton Laboratory, Bristol.

THE powdered nut of *Areca Catechu* is largely used in veterinary practice as a tœnicide, and is in especial favour with those amateurs who are accustomed to treat their own dogs for an attack of worms. Cases of poisoning following its use are rare, and the following particulars of one which has recently been met with in ordinary analytical practice are therefore communicated.

A teaspoonful of areca nut in fine powder (about 56 grains) was added to half a teacupful of castor oil, and administered to four Dachshund puppies of the same litter aged five months. So far as can be ascertained the substances were thoroughly mixed, and approximately equal amounts given to each. All the dogs were highly bred and in fairly good health previously. In less than five minutes after administration they were seen to be in distress. They had great difficulty in breathing, coughed slightly, and fell down on one side. Locomotion was only possible with difficulty. Seeing their condition the owner endeavoured to administer salt and water as an emetic. This was successful in two cases, but not in the others. The latter gradually got weaker, became unable to rise, and died in ten minutes. No convulsions or convulsive twitchings occurred. Respiration gradually became more and more difficult until death quietly ensued, intelligence being maintained until the end. The bowels were not moved. A third dog died after languishing for five hours, notwithstanding the successful administration of the emetic.

On post-mortem examination the stomach was found to be slightly inflamed, the inflammation being general and not in patches. The trachea and some of the lung passages were filled with a dense white froth. The left ventricle was found gorged with blood, as was also the aorta and left auricle. The right auricle and ventricle were comparatively empty. The other organs were normal. The iris showed no alteration from its normal size.

The contents of the stomach were extracted with weak alcohol and dilute acetic acid, and the usual tests for the more commonly occurring alkaloids applied. (This was done because the owner, who has been in the habit of frequently giving areca nut to his dogs, was of opinion that that substance could not be the cause of death, but that some more powerful poison must be present). None of these were found, but Mayer's reagent gave an alkaloidal precipitate with the extract. The amount of substance available was, however, so small that beyond this no confirmation of the presence of the arecoline—the poisonous alkaloid in areca nut—was possible. The whole circumstances of the case, as well as the absence of the other alkaloids and mineral and other poisons, all of which were unsuccessfully tested for, can leave no doubt that death was caused by the nut.

Assuming that each dog had an equal quantity, the amount was approximately 14 grains. It is, however, quite a common thing for doses of a drachm (60 grains) to be administered without ill effect.

It would thus appear that the action of the substance is uncertain, and that its employment therefore requires great care.

It should be mentioned that the unused portion of the sample was sent for analysis and thoroughly examined, but no poisonous substance other than that in the areca nut could be discovered.

## USE OF
## THE X RAYS FOR ANATOMICAL RESEARCH: ANGEIOLOGY, DEVELOPMENT, OSSIFICATION, EVOLUTION OF TEETH, &c.

By CH. REMY and G. CONTREMOULINS.

WE have the honour of submitting to the Academy a series of radiographs taken on the dead body, in which we observe anatomical details not hitherto recognised. We wish to speak of the disposition of the arterial system down to its finest sub-divisions.

In the figure, which represents the hand with its fore-arm and a part of the arm, we may follow in their relations with the osseous system the divisions of the arteries, the collaterals of the fingers up to the vascular tufts of the digital pulp. We may also follow the penetration of the arteries into the bony tissue.

In the parts which we have submitted to radiography the veins are not apparent, but we may obtain their image by the procedure which we have made use of.

Professor Marey has suggested to us the idea of rendering the vascular system opaque to the X rays by injecting them with a liquid holding in suspension impalpable metallic powders; a great variety of such powders are now met with in commerce under the name of bronzes. The medium which we employed is common sealing-wax dissolved in alcohol; the injection is performed in the cold.

We emphasise the importance of the results of this method, which gives the distribution of the vessels with their real situation and relations which are always altered by dissection. In order to seize the different degrees of depth of the vascular planes we have employed stereoscopic proofs, the aspect of which is striking.

In the same figures, thanks to the Collardeau tube and the Gaiffe coil, the outlines are perfectly distinct as well as the details of the structure of the bones.

One of our figures represents the lower half of the body of a human fœtus on which the position of the points of ossification is very well determined.

In another figure, representing the half of the lower jaw of a child of 7 years, we see distinctly the four molars with their layer of enamel, the dentine, the dentary pulp, and the channels of the nerves; whilst at the base of the ascending branch the wisdom-tooth, in its closed cell, awaits the time of its appearance.—*Comptes Rendus*, cxxiii., p. 711.

## AN ATTEMPT TO DETERMINE THE ADIABATIC RELATIONS OF ETHYL OXIDE.*

By E. P. PERMAN, D.Sc., W. RAMSAY, Ph.D., F.R.S., and J. ROSE-INNES, M.A., B.Sc.

THE wave-length of sound in gaseous and in liquid ethyl oxide (sulphuric ether) has been determined by the two first-mentioned of the authors, by means of Kundt's method, between limits of temperature ranging from 100° C. to 200° C., and of pressure ranging from 4000 to 31,000 m.m. of mercury, and of volume ranging from 2·6 c.c. per grm. to 71 c.c. per grm. Making use of the same apparatus throughout, the results obtained are to be regarded as comparative, and, by careful determination of the pitch of the tone transmitted through the gas, it is probable they are approximately absolute.

* Abstract of a Paper read before the Royal Society, Dec. 10, 1896.

The sections of the complete memoir deal with (I.) a description of the apparatus employed, (II.) the method of ascertaining the weights of ether used in each series of experiments, (3) determinations of the frequency of the vibrating rod, (IV.) the calculations of the adiabatic elasticity and tables of the experimental results, and (V.) a mathematical discussion of the results. The last section is due to Mr. Rose-Innes.

As the theoretical results are of interest, a brief outline of them may be given here.

It will be remembered that one of the authors, in conjunction with Dr. Sydney Young, showed that for ether, and for some other liquids, a linear relation subsists between pressure and temperature, volume being kept constant, so that—

$$p = bT - a.$$

It has been found that a similar relation obtains between adiabatic elasticity and temperature, volume, as before, being kept constant: so that, within limits of experimental error, where E stands for adiabatic elasticity,—

$$E = gT - h,$$

$g$ and $h$ being functions of the volume only. Between these two equations, we may eliminate T, and so express E as a linear function of $p$, volume being kept constant. The coefficient of $p$ in such an equation would be $g/b$, and this fraction, on being calculated from the data available, proves to be nearly constant. For working purposes it is assumed that $g/b$ may be treated as strictly constant, and it is shown that this assumption does not introduce any serious error within the limits of volume considered. We then find it possible to integrate the resulting differential equation, and the complete primitive enables us to draw a set of adiabatic curves. We believe that this is the first time adiabatic curves have been obtained for any substance except perfect gases.

A mathematical discussion is added as to what extent the equations—

$$E = gT - h$$

and—

$$g/b = \text{constant},$$

can be considered as strictly true, and not merely approximate.

The experimental results for liquid ether form an appendix to the paper.

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## A METHOD FOR THE SEPARATION OF ALUMINUM FROM IRON.

### By F. A. GOOCH and F. S. HAVENS.

Of the well-known methods for the separation of aluminum from iron—by the action, for example, of an alkaline hydroxide in aqueous solution, or by fusion of the mixed oxide in potassium or sodium hydroxide; by reduction of the iron oxide to the metal by heating in hydrogen, with the subsequent solution of the metallic iron in hydrochloric acid; by boiling the nearly neutral solution of the salts of aluminum and iron with sodium thiosulphate either with or without sodium phosphate; by acting with hydrogen sulphide or ammonium sulphide upon solutions of the salts containing also an ammoniacal citrate or tartrate—no single process can be said to be ideal as regards directness, rapidity, and accuracy of working. We have deemed it not superfluous, therefore, to attempt the utilisation of a reaction which should apparently be capable of effecting directly and quickly the separation of aluminum from iron under conditions easily attainable.

It is known (Gladysz, *Ber. d. d. Chem. Gesell.*, xvi., 447) that the hydrous aluminum chloride $AlCl_3 \cdot 6H_2O$ is very slightly soluble in strong hydrochloric acid, while ferric chloride, on the other hand, is extremely soluble in that medium. It is this difference of relation of which we wished to take advantage.

It appeared at the outset that crude aluminum chloride could be freed from every trace of a ferric salt by dissolving it in the least possible amount of water, saturating the cooled solution with gaseous hydrochloric acid, filtering upon asbestos in a filtering crucible or cone, and washing the crystalline precipitate with the strongest hydrochloric acid. Aluminum chloride prepared in this way gave no trace of colour when dissolved in water and tested with potassium sulphocyanide. The correlative question as to how much aluminum chloride goes into solution under the conditions was settled by taking a portion of the pure aluminum chloride, dissolving it in a very little water, diluting the solution with strong hydrochloric acid, saturating the cooled liquid with the gaseous acid, filtering on asbestos, precipitating by ammonia the aluminum salt in the filtrate, and weighing the ignited oxide.

From 10 c.m.$^3$ of such a filtrate we obtained in two determinations 0·0022 grm. and 0·0024 grm. of the oxide, the mean of which corresponds to 23 parts of the oxide, or 109 parts of the hydrous chloride in 100,000 parts of the strong hydrochloric acid. This degree of solubility, though inconsiderable when the objective point is the preparation of the pure salt of aluminum, is obviously incompatible with the attainment of quantitative accuracy in the retention of the aluminum. We have found, however, that various mixtures of anhydrous ether and the strongest hydrochloric acid can be used satisfactorily as solvents for the iron chloride, while the aluminum chloride is insoluble to a very high degree in a mixture of hydrochloric acid and ether taken in equal parts and thoroughly saturated with gaseous hydrochloric acid at the atmospheric temperature. We found that 50 c.m.$^3$ of the solution of aluminum chloride, obtained by mixing about 0·1 grm. of the hydrous chloride (dissolved in 2 c.m.$^3$ of water) with the mixture of pure, specially prepared aqueous hydrochloric acid and ether in equal parts, and again saturating the liquid at 15° C. with gaseous hydrochloric acid, left upon evaporation and ignition 0·0004 grm. in each of two experiments—results which indicate a maximum solubility corresponding to 1 part of the oxide or approximately 5 parts of the chloride in 125,000 parts of the equal mixture of ether and aqueous hydrochloric acid of full strength.

Pure aqueous hydrochloric acid of full strength mixes perfectly with its own volume of anhydrous ether, but it is a curious fact that the addition to this mixture of any very considerable amounts of a solution of ferric chloride in strong hydrochloric acid determines the separation of a greenish oily ethereal solution of the ferric salt upon the surface of the acid. The addition of more aqueous acid does not change the conditions essentially, but more ether renders the acid and the oily solution completely miscible. The ferric chloride seems to abstract ether from the ether-acid mixture and, then dissolved in the ether, remains to some extent immiscible with the aqueous acid thus left until the addition of more ether restores to the mixture that which was taken from it by the ferric chloride. Our experiments show that, while for the separation of insoluble aluminum chloride from certain small amounts of soluble ferric chloride, the mixture of the strongest aqueous hydrochloric acid and ether in equal parts serves a most excellent purpose, when larger amounts of ferric chloride are to be dissolved ether must be added proportionately in order to prevent the separation of the ethereal solution of ferric chloride from the rest of the liquid.

Great care was taken to insure the purity of the aluminum chloride used in the test experiments. The so-called pure chloride of commerce was dissolved in the least possible amount of water, and this solution was treated with a large volume of strong hydrochloric acid,

The chloride thus obtained, free from iron, but possibly contaminated (as we found by experience) with some alkaline chloride, was dissolved in water and converted by ammonia to the form of the hydroxide, which was thoroughly washed and dissolved in hot hydrochloric acid of half-strength. From this solution, after cooling, gaseous hydrochloric acid precipitated the hydrous chloride in pure condition. The chloride thus prepared was dissolved in water, and the strength of the solution was determined by precipitating the hydroxide from definite portions, and weighing the ignited oxide in the usual manner.

TABLE I.

| | $Al_2O_3$ taken in solution as the chloride. Grm. | $Al_2O_3$ found. Grm. | Final volume. C.m.$^3$. | Error. Grm. |
|---|---|---|---|---|
| 1. | 0·0761 | 0·0746 | 50 | 0·0015 − |
| 2. | 0·0761 | 0·0745 | 50 | 0·0016 − |
| 3. | 0·0761 | 0·0741 | 50 | 0·0020 − |
| 4. | 0·0761 | 0·0734 | 50 | 0·0027 − |
| 5. | 0·0761 | 0·0756 | 50 | 0·0005 − |
| 6. | 0·0157 | 0·0149 | 45 | 0·0008 − |
| 7. | 0·0157 | 0·0147 | 40 | 0·0010 − |
| 8. | 0·0157 | 0·0144 | 45 | 0·0013 − |
| 9. | 0·0480 | 0·0481 | 30 | 0·0001 + |
| 10. | 0·0960 | 0·0957 | 30 | 0·0003 − |

In the experiments recorded in Table I., measured portions of the standardised solution were submitted to the treatment with hydrochloric acid and ether. The essential thing in the process is to have at the end a mixture of the strongest aqueous hydrochloric acid with an equal volume of anhydrous ether saturated at a temperature of about 15° C. The most convenient way to secure these conditions seems to be to mix the aqueous solution of the aluminum salt with a suitable volume of the strongest aqueous hydrochloric acid—enough to make the entire volume something between 15 and 25 c.m.³— to saturate this mixture with gaseous hydrochloric acid, while the liquid is kept cool by immersing the receptacle containing it in a current of running water, to intermix a volume of ether equal to the volume of the liquid, and finally, to treat the ethereal mixture once more with the gaseous acid to insure saturation. The precipitated crystalline chloride was collected upon asbestos in a perforated crucible, washed with a previously prepared mixture of hydrochloric acid and ether carefully saturated with the gaseous acid at 15° C., and either ignited after careful drying at 150° or re-dissolved in water, converted to the hydroxide by ammonia in the usual way and weighed as the oxide after filtration, washing, and ignition. In Experiments 1 to 4 the precipitated chloride was ignited directly; in Experiment 5 the ignition was made with great care in an atmosphere of superheated steam; and in Experiments 6 to 10 the chloride was dissolved, precipitated as the hydroxide, and weighed as the oxide.

The experiments in which the chloride was converted to the hydroxide before ignition show upon the average an absolute loss of about 0·0006 grm.; the single experiment in which the ignition took place in steam shows about the same loss—0·0005 grm.; while in those experiments in which the chloride was dried and then ignited directly, the average loss amounts to about 0·0020 grm. The error of the process which involves the precipitation of the aluminum as the hydroxide, falls within reasonable limits, but is plain that the direct ignition of the chloride is liable to error, which may possibly be explicable as a mechanical loss occasioned by the too rapid evolution of the hydrochloric acid and water of crystallisation, or, possibly, as the result of a very slight volatilisation of the aluminum still holding chlorine in spite of the decomposing action of the water upon the chloride. In either case, it would seem to be reasonable to suppose that a layer of some easily volatilisable oxidiser placed upon the aluminum chloride might serve to obviate the diffi-

culty—in the one case, by serving as a screen to diminish mechanical transportation of the non-volatile material; and in the other, by acting as an agent to promote the exchange of chlorine for oxygen on the part of the aluminum chloride.

We have tried, therefore, the expedient of covering the aluminum chloride before ignition with a layer of mercuric oxide, which of itself left no appreciable residue when it volatilised. The hydrous chloride was collected as usual upon the asbestos in a perforated crucible, dried for a half-hour at 150° C. covered with about 1 grm. of the pure mercuric oxide, gently heated with great care under a suitable ventilating flue, and finally ignited over the blast. The results are given below:—

TABLE II.

| | $Al_2O_3$ taken in solution as the chloride. Grm. | $Al_2O_3$ found by ignition with HgO. Grm. | Final volume. C.m.$^3$. | Error. Grm. |
|---|---|---|---|---|
| 1. | 0·0761 | 0·0758 | 25 | 0·0003 − |
| 2. | 0·0761 | 0·0754 | 25 | 0·0007 − |
| 3. | 0·0761 | 0·0751 | 25 | 0·0010 − |

It is obvious, therefore, that the precipitation of the crystalline hydrous aluminum chloride from solutions of the pure salt is perfectly feasible and very complete, when effected by aqueous hydrochloric acid and ether thoroughly saturated with the gaseous acid and kept cool; and that the conversion of the chloride into the weighable form of the oxide is best effected by ignition under a layer of mercuric oxide, or by dissolving it in water and precipitating it as the hydroxide, to be afterward washed, dried, and ignited. Of the two methods the former is by far the more convenient.

The precipitation of the aluminum chloride in pure condition from solutions containing ferric chloride ought not, it would seem, to present any difficulty, providing only that the precaution is taken to have present a sufficient excess of ether. The question was put to the test of experiment with the results recorded in Table III.

Measured portions of the standardised solution of aluminum chloride were evaporated nearly to dryness in a platinum dish, an amount of pure ferric chloride equivalent to about 0·15 grm. of the oxide was added in a very little water, 15 c.m.³ of the mixture of strong hydrochloric acid and ether in equal parts were introduced, the liquid was saturated at 15° C. with gaseous hydrochloric acid (the dish being held in a convenient device for cooling it by running water), 5 c.m.³ more of ether were added to secure complete miscibility of the solutions, and more gas passed to perfect saturation. The aluminum chloride was collected upon asbestos in a perforated crucible, washed with a mixture of ether and aqueous hydrochloric acid thoroughly saturated with the gaseous acid, dried at 150° C. for a half-hour, covered with 1 grm. of pure mercuric oxide, and ignited at first gently, and finally over the blast.

TABLE III.

| | $Al_2O_3$ taken in solution as the chloride. Grm. | $Al_2O_3$ found by ignition with HgO. Grm. | $Fe_2O_3$ present as chloride. Grm. | Final volume. C.m.$^3$. | Error. Grm. |
|---|---|---|---|---|---|
| 1. | 0·0761 | 0·0757 | 0·15 | 25—30 | 0·0004 − |
| 2. | 0·0761 | 0·0756 | 0·15 | 25—30 | 0·0005 − |
| 3. | 0·0761 | 0·0755 | 0·15 | 25—30 | 0·0006 − |
| 4. | 0·0761 | 0·0755 | 0·15 | 25—30 | 0·0006 − |

The results show plainly a very satisfactory limit of error.

Determination of the Colouring Power of Litmus. —E. Dieterich (*Helfenberg Annalen*).—The author grinds up 5 grms. of the specimen with 80 c.c. of water, rinses into a 100 c.c. flask, digests at 50° for two hours, lets cool, and filters after settling. 0·05 c.c. of the filtrate, diluted with 100 c.c. of water, must appear distinctly coloured if viewed from above in a stratum of 20 c.m. in thickness.

## THE PERMEABILITY OF VARIOUS ELEMENTS TO THE RÖNTGEN RAYS.

By JOHN WADDELL, B Sc.( Lond.), Ph.D. (Heidelberg), Professor of Chemistry, Royal Military College of Canada.

THE following experiments were undertaken with the object of ascertaining whether fluorescent substances are specially opaque to the X rays, in accordance with the well-known laws of absorption illustrated by the Fraünhofer lines in the spectrum.

The investigation thus begun was extended to a number of substances whose permeability to the rays was tested, in order to discover whether any law of general application were apparent.

Barium platinocyanide, thinly laid on paper, was first photographed, and found to hinder the transmission of the rays, and the degree of opacity was sensibly the same whether the fluorescent substance was in direct contact with the photographic film or separated from it by several thicknesses of paper. This experiment was tried shortly after Röntgen's discovery was announced; it was known, however, that platinum was opaque, and that barium was also probably opaque.

A number of substances—some fluorescent, others not—were then taken in the form of powder, made into heaps of about the same thickness, and exposed to the rays. Uranic acid, uranic nitrate, tungstic acid, molybdic acid, sulphate of quinine, barium nitrate, and potassium nitrate were thus photographed on one plate. The sulphate of quinine was apparently perfectly transparent, as no trace of its presence was seen when the negative was developed; the other substances appeared about equally opaque.

As it seemed that fluorescence had little influence one way or the other, the investigation turned chiefly to a comparison of similar compounds of different metals. At first equal weights—0·2 grm.—of substance, in small cylindrical pasteboard pill-boxes, were worked with, but no very definite result was arrived at except that magnesium carbonate was much more transparent than any of the other substances, being comparable in this respect with many organic bodies. Such small quantities of powders were not easily spread in layers of uniform thickness, and thus the photographs were blotched.

From this time on one of Newton and Co.'s focus tubes was used and larger quantities of substances were used, and the time of exposure varied from fifteen seconds to seven minutes.

It had been stated by some observers that the opacity of metals is proportional to their densities, and it would follow from this statement that, if the thicknesses of the metal taken were inversely proportional to their specific gravities, they should be equally opaque.

In my further experiments oxides or carbonates of the opaque element were taken in such quantities that in each box there was 1 grm. or one $\frac{1}{2}$ grm. of the opaque element, which was usually a metal, and which will be so designated in the remainder of this article.

The oxides of molybdenum, tungsten, uranium, silicon, lead, and tin contained 1 grm. of metal; the carbonates of the alkaline earths—because more bulky—were taken in half the proportionate amount.

It was thought that, by varying the lengths of exposure in different experiments, a difference might be detected between the different substances; that with *some* length of exposure the opacity might show different. With a very short exposure it was possible that some of the substances would allow no appreciable amount of the radiations to pass through, while others would transmit some of the rays. There was very little difference between the different substances as regards the shadow cast on the photographic plate, and this might seem to substantiate the idea that the opacity of the metals is proportional to their densities, except that the carbonates containing $\frac{1}{2}$ a grm. of metal were not noticeably different from the com

pounds containing a grm. of metal. No conclusions could therefore be drawn from the experiments thus far described.

I have given so full an account of these unsuccessful experiments because I believe that many of the observations recorded have been open to just the kind of uncertainties I have mentioned. Where the metals can be beaten out thin it may be all right to test their opacity in a manner similar to the above, but in other cases the result is misleading.

All of the above experiments may be regarded as attempts to compare the *opacities* of the different metals, but these are so great that in the short exposure they all appear equal; hence I determined to compare the *transparencies*,—that is, instead of having the photographic plate exposed except when covered by the substances, I protected the sensitive film by a sheet of lead, about an eighth of an inch thick, in which holes were punched small enough to be covered by the boxes containing the powders. I chose for experiment the oxides and carbonates of the various groups of metals—Mo, W, Ur; Si, Sn, Pb; Mg, Zn, Cd; Ca, Sr, Ba; and Li, Na, K,

In addition I took photographs of the carbonates of nickel and cobalt, and of the oxide of copper.

The time of exposure ranged from fifteen minutes to nearly an hour. The weights of the lithium, sodium, and potassium carbonates used contained 0·5 grm. of metal, because the larger quantity could not be put in the boxes; they were compared with calcium carbonate, which also contained 0·5 grm. of metal, while double the amount of calcium carbonate in another box was compared with the other compounds which also contained a grm. of the metal. There was very little difference between the lithium and sodium carbonates, which were much more transparent than the potassium carbonate, while this last was of appreciably the same transparency as the calcium carbonate containing the same amount of metal.

In the next group the calcium carbonate was much more permeable than the strontium or barium carbonates, —so much so that I thought the permeability of the calcium and barium might be inversely proportional to the atomic weights; I therefore compared the permeability of a quantity of barium carbonate containing $\frac{40}{137}$ grm. of barium with that of a quantity of calcium carbonate containing 1 grm, of calcium, and found the former greater than the latter, so that the idea suggested above had to be abandoned. In any case such a relationship between the metals could have been accidental only, since strontium carbonate is no more permeable than barium carbonate,

Zinc carbonate was slightly more permeable than the barium carbonate, and naturally far inferior in transparency to magnesium carbonate. Cadmium oxide was a little less permeable than the zinc compound, and about equal to tungstic acid ($WO_3$), which was if anything a shade more permeable than the corresponding compounds of molybdenum and uranium, containing the same amount of metal. In all of these cases, however, the photographic effect was slight, and was visible on the negative only when held in a favourable position.

In the group which consisted of silicon, tin, and lead, it was found that the oxide of the first member was far more permeable than that of either of the others, which were more nearly alike and approached much nearer the other heavy metals.

Nickel and cobalt carbonates and copper oxide are as nearly as possible equal to tungstic acid.

As the result of the above experiments, it is evident that there is no universal connection between the density of the metal and its opacity, because lithium and sodium carbonates are both much more permeable than potassium carbonate, while the specific gravity of potassium is between that of lithium and sodium. On the other hand, it is not in proportion to the atomic weight, for sodium carbonate is not less, but slightly more, permeable than lithium carbonate, as well as much more permeable than potassium

carbonate. In the same way strontium carbonate is not midway between calcium and barium carbonates.

With the heavier metals the opacity seems to be nearly in proportion to the density, but for those metals that cannot be obtained in very thin plates it is difficult to speak with certainty, since they are all so opaque.

It was because the metals themselves could in many cases not be experimented with that I had used the oxides and carbonates, but I tested the permeability of potassium, sodium, magnesium, and aluminium.

The two alkali metals were enclosed in paraffin wax, and were 3·9 m.m. thick; the aluminium and magnesium were 1·5 m.m. thick. The magnesium was more permeable than the aluminium, and much more permeable than the potassium, though not so permeable as the sodium. There was nearly the same relation between the opacities of the potassium and sodium in the metallic state and in the form of carbonate.

In one of the experiments described above the permeability of calcium fluoride was compared with that of calcium carbonate containing the same amount of metal, and found to be about equal to it. This was a still more conclusive proof that fluorescence does not increase the impermeability of the substance. The fact, moreover, suggested to me that all the permeable elements had proved to be of low atomic weights.

I therefore decided to compare fluorine with chlorine, bromine, and iodine; and for that purpose used the sodium salts, and took quantities containing ½ a grm. of the halogen. The advantage of the sodium salt was that sodium had proved to be tolerably permeable, and I was at all events certain that, if the fluoride proved to be more transparent than the other salts, fluorine must be still more transparent than the other halogens, because it contained so much greater quantity of metal. Sodium fluoride contains more sodium than fluorine, while sodium iodide does not contain one-fifth as much.

On the same photographic plate I had boracic acid containing ½ a grm. of boron, and a piece of sheet aluminum whose weight for the same cross section was one-third of a grm.

Unfortunately in this experiment I did not have the same induction-coil as before, but was compelled to use a much smaller one giving a spark of less than ½ an inch in length, and, though I gave an exposure of over four hours, the chloride, bromide, and iodide did not permit of any photographic effect on the sensitive film. I am therefore unable to say whether there would have been any difference shown between these salts if I had had a more powerful coil; but it was clearly demonstrated that fluorine is more permeable than the other halogens, because the photographic effect through over a grm. of the sodium fluoride (corresponding to 0·5 grm. of fluorine) was only a little inferior to that through one-third of a grm. of aluminium. I may add that quite a perceptible effect was produced by the radiations passing through copper foil about 0·05 m.m. in thickness.

The boracic acid was not so permeable as the sodium fluoride. The total weight of the former was over twice as much as that of the latter; and it is quite possible that part of the opacity was due to the oxygen, and that the permeability of boron is greater than appeared in the experiment, and probably superior to that of aluminium.

I have not tried the permeability of beryllium; but Capt. Cochrane (Instructor in Physical Science in the Royal Military College of Canada), in the course of an investigation on the relative permeability of real and imitation gems, found that beryl is transparent. All of the real gems thus tested, with the exception of garnet, were quite permeable, and garnet was the only one containing a heavy metal (iron).

Though, in the experiment spoken of a few sentences back, the radiations were not effective through sodium chloride, I had in one of the earlier experiments a crystal of halite of same cross section as calcium carbonate powder in the box. The halite weighed 1·5 grms. and the

calcium carbonate 1·25 grms., and the permeability was almost exactly equal. Of the halite the more opaque element is the chlorine, and it seems to be more permeable than calcium or potassium.

On the same negative, the transparency of a selenite crystal weighing 0·85 grm. was considerably greater than that of the calcium carbonate, and as closely as I could judge it was about equal to that of the same amount of carbonate. The proportion of calcium in selenite is less than in calcium carbonate, and therefore part at least of the opacity is contributed by the sulphur; but probably the latter is more permeable than chlorine.

I give these data because I have not now at hand the apparatus for making the more decisive test, which would be to compare the permeability of sulphur with that of aluminium on the one hand and of sodium chloride on the other.

The experiments I have described make it evident that the elements may be divided, so far as permeability is concerned, into two classes,—those of low atomic weight and those of higher atomic weight,—the transition taking place between the atomic weights 30 and 40. Among the higher elements the opacity is probably not far from being proportional to density, but with the elements of low atomic weight the same law does not hold; sodium, for instance, is decidedly more permeable than aluminium, because in the experiment above mentioned the thicknesses of the two metals were approximately inversely as their densities. Lithium and sodium are more nearly alike.

Metals and non-metals cannot be differentiated from each other; boron is less permeable than sodium, and sodium is less permeable than oxygen.

One is naturally led to speculate as to the reason of the greater permeability of substances of low atomic weight. Until our knowledge of the phenomena connected with Röntgen rays is more definite, hypotheses must be vague; but the suggestion readily occurs to one that the atoms of low weight are simpler in structure, and impede the motions of the ether to a less extent than do the atoms of high weight. This, on the assumption that the ether is the medium of transmission of the Röntgen radiation. If, however, matter be the vehicle of transmission of energy, the transparency may be due to the greater ease with which atoms of small weight are set in motion.

*Addenda.*—In comparing the relative permeability of crystals and the same mineral powdered, I found that the photograph of the latter, though otherwise similar to that of the former, showed a granulated appearance. This was also the case with many of the powders. I thought that it might be due to the powder being in little more or less coherent lumps; but precipitated silica, which had such a thickness that more than 2 grms. of it were in the little box,—a thickness of, say, three-quarters of an inch, —showed the same granulation.

The calcium carbonate did not exhibit it, however, nor did the zinc carbonate or sodium carbonate.

I do not know whether the idea has been universally abandoned, that the photographic effect is due to the fluorescence of the Crookes tube; but the fact that when the sensitive plate is exposed to the rays from different sides of the tube the photographic effect is vastly different seems to me fatal to such an hypothesis. When, with the focus tube, the plate is so situated that *light*, starting from the cathode and reflected by the anode, would be reflected to the plate, the photographic effect is far greater than if the tube is rotated into any other position, say at right angles to the former one. A similar phenomenon is shown if the tube be used to discharge a gold-leaf electroscope. This is not due to difference of distance from the most fluorescent part of the tube; nor is it due to the radiations going through more glass when the Crookes tube is inverted. I have taken photographs through two thicknesses of glass, in the ordinary dry plates, and have found them quite distinct.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.
### *Ordinary Meeting, December 3rd, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. James Herbert Brown, Dallas Place, Lancaster; John Wallis Dodgson, B.Sc., 47, Hirwain Road, Aberdare, Glamorgan; Lawrence Dufty, 33, Broomhall Place, Sheffield; Joseph Lake Gibbons, West Carlton Street, Blyth; Alexander William Gilbody, M.Sc., Ph.D., Owens College, Manchester; Harold Walter Gough, B.A., 73, Billing Road, Northampton; Ernald George Justinian Hartley, B.A., Wheaton Aston Hall, Stafford; Charles Henry Martin, 14 Aldred Street Crescent, Salford; William James Stainer, B.A., 3, Havelock Road, Stanford Avenue, Brighton; Samuel Matthew Walford, 62, Bloom Street, Stockport; James Wallace Walker, M.A., Ph.D., University College, London.

The following were duly elected Fellows of the Society: Henry Edward Aykroyd, William Ballingall, M.A., Gopal Chandra Bauerfee, Charles Bathurst, B.A., Lauritz Hansen Bay, Charles Edward Browne, B.Sc., Walter William Cobb, M.A., George Harold Cross, B.Sc., William Duncan, Walter John Elliott, M.A., Eric David Ewen, John Thomas Fleet, George George, Arthur Croft Hill, B.A., Charles Alexander Hill, John William Hinchley, William Trevor Lawrence, B.A., Robert Dexter Littlefield, Thomas Henry Lloyd, Thomas William Lockwood, Hugh Manners, M.A., B.Sc., Edward Seaborn Marks, Arthur Stanley Mayfield, William M. Miller, Landon Clarence Moore, Francis Ambrose Moss, Herbert William Moss, Joseph Terrence de la Mothe, Alexander Henry Mitchell Muter, William Harrison Pearsall, Henry William Potts, Frederick Belding Power, Ph.D., William Russell, Arthur Edwin Saville, Herbert Cecil Seabrooke, Kotaro Shimomura, B.Sc., William Horace Sodeau, B.Sc., Charles Thompson, B.Sc., William Henry Walker, William Watson, M.A., Edwin Whitfield Wheelwright, B.A., Ph.D., John Inctus Whimster, John Harrison Wigner, Ph.D., Alfred James Wilcox.

Of the following papers those marked * were read:—

*156. "*Constitution and Colour.*" By ARTHUR G. GREEN.

In a scheme for the qualitative analysis of the coal-tar colouring-matters published in 1893 (*J. Soc. Chem. Ind.*, 1893, xii., 3), the author pointed out that the leuco-compounds of various dye-stuffs exhibit a striking difference of behaviour on exposure to air. Leaving out of account those which are completely split up by reduction (viz., azo-, nitro-, and nitroso-colours), it is possible, by means of this reaction, to classify colouring-matters into two groups, viz.:—I. Colours whose leuco-compounds are not easily re-oxidised on exposure to air. II. Colours whose leuco-compounds are rapidly re-oxidised on exposure to air.

Group I. comprises all the colouring-matters of the triphenyl-methane series, the phthaleins or pyrone colours, indophenols, and indamines. Group II. comprises the indigo class, the azines, azonium colours, oxazines, thiazines, acridine colours, thiazol colours, quinoline colours, oxyanthraquinone colours, and certain colouring-matters of unknown constitution.

In explanation of the cause underlying this difference of behaviour, the author, in 1892, put forward the suggestion (*Proc.*, 1892, viii., 195) that, assuming the correctness of the "quinonoid" theory of colour (Armstrong (*Proc.*, 1888, iv., 27; 1892, viii., 101, 143, 189, and 194; 1893, ix., 52 and 206), the colouring-matters of the first group might be regarded as *para-quinonoid,*—



of the second group as *ortho-quinonoid,*—
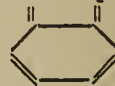


In the present paper this view is more fully discussed, and further evidence is brought forward in confirmation of it.

An examination of the members of the two groups shows that, whilst nearly all the colouring-matters of Group I. are compounds substituted in the para-position alone, no plain para-substituted compounds are found in Group II.; on the other hand, whilst Group II. contains compounds substituted in the ortho-position alone (*e. g.*, indigo) and compounds substituted in both positions, no plain ortho-substituted compounds are to be found in Group I. Therefore, if the "quinonoid" theory of colour be accepted, it follows that dye stuffs, which, from their constitution, must be ortho-quinonoid, only occur in Group II., whilst those which must be para-quinonoid, only occur in Group I.

In Group I. the theory agrees in all cases with the usually accepted constitution of the colours. In Group II., when it is not in accord with the usually accepted view, the ortho-quinonoid formulæ give as good, or better, interpretations to the properties of the colouring-matters than the para-quinonoid formulæ previously assigned them.

It would be anticipated, from the well-known interrelationship of ortho-substituents, that two groups occurring in an ortho-position to each other would have a greater tendency to enter into a more intimate union, and therefore would be more oxidisable than if they stood in the para-position.

The stability towards acids of the colouring-matters of the methylene-blue and safranine series, and the oxidisability of their leuco-compounds, compared with the extreme instability to acids of the parent indamines (paraquinone-imides) and non-oxidisability of their leuco-compounds, forcibly suggest a change of type.

The tendency exhibited by many azines and oxazines to form amido-derivatives by addition, as in the case of Meldola's blue, can only receive an explanation by the assumption of an ortho-quinonoid structure, since, in the naphthalene nucleus, where the substitution takes place, a para-quinonoid structure is not possible.

### DISCUSSION.

Dr. KIPPING said that Mr. Green's classification of certain dye-stuffs into derivatives of ortho- and of para-quinones respectively, being based solely upon the rapidity with which the corresponding leuco-compounds undergo aërial oxidation, it would add to the interest of his communication if he could define more exactly the words "easily oxidised" by introducing the element of time; for the rapidity of oxidation of all the leuco-compounds of one class would probably not be the same, and consequently those reduction products of paraquinones which oxidised most easily might do so more rapidly than the leuco-compounds of some of the orthoquinones. Should this never, or rarely, occur, Mr. Green's classification would be extremely useful; but as it does not even include all dye-stuffs, it cannot be regarded as affording any support to the view held by Dr. Armstrong, namely, that *all* coloured carbon compounds have a quinonoid structure. This view, attractive though it may be, and supported by the numerous examples which have been brought under notice, is nevertheless untenable: that all quinones and their derivatives are coloured may be true, but to assume that all coloured substances are quinones would necessitate in many cases the adoption of constitutional formulæ utterly at variance with chemical facts. Without discussing the meaning of the somewhat vague word "colour," it may be pointed out that the colour of a substance depends, amongst other conditions, on its crystalline structure. In the course of some work carried out with Mr. Revis, it was noticed that isonitrosohydrindone

forms a yellow sodium derivative, the colour of which depends on the temperature at which it is crystallised; when heated at 70—80° the yellow salt is rapidly converted into a scarlet modification, owing to a change in crystalline form taking place. Numerous examples of a similar kind are known, and taking this fact into consideration, and having regard more especially to the number of undoubted exceptions to Dr. Armstrong's colour rule, it is impossible to accept his generalisation in its present form.

Mr. LING agreed in considering that the quinone theory was not established as a general rule.

Dr. ARMSTRONG thought that Mr. Green's generalisation was of considerable value as a working hypothesis, but he was inclined to doubt whether it would be possible by means of such a test as that suggested to sharply divide dye-stuffs into two classes; it was rather to be expected that the members of the two classes would merge gradually into each other. As the method would in many cases incite the further investigation of structure, which was so much to be desired, it must prove to be of considerable service. As to the alternative formulæ suggested by Mr. Green, he could not regard them as satisfactory on the whole; the representation of oxygen as a tetrad in such a case as that of Meldola's blue, for example, appeared to him to involve conclusions beyond the bounds of probability. Mr. Green had spoken of the Armstrong-Nietzki quinonoid theory of colour: unaccustomed as he was to put forward claims of priority, he could not help remarking that although Nietzki had undoubtedly called attention to the occurrence of quinonoid structure in many colouring-matters, he had never attempted to generalise. He, the speaker, had, however, endeavoured to extend the hypothesis not only to colouring-matters, but to coloured substances generally, and had given a definition of the term quinonoid, which included even substances such as iodoform. No doubt the difficulties to be overcome were very great, and it would be long before we should be able to explain all cases of the occurrence of colour; meanwhile all we could do was to patiently investigate the facts.

Mr. GREEN, in reply, wished it to be understood that he regarded the quinone theory as affording a satisfactory explanation of the colour of organic dye-stuffs, though not of the colour of all coloured organic compounds.

*157. "Derivatives of α-Hydrindone."* By C. REVIS and F. STANLEY KIPPING, Ph.D., D.Sc.

As α-hydrindone and camphor are in some respects analogous to constitution (inasmuch as each contains two closed carbon chains, in one of which occurs the group –CH₂·CO– ), the behaviour of the two ketones and of corresponding derivatives has been studied, in order to ascertain to what extent they would show analogous reactions; it has thus been found that, except in a few instances, there is a marked difference in chemical behaviour.

α-Hydrindoneoxime, for example, behaves quite unlike camphoroxime when heated with mineral acids, as it yields the two condensation products (anhydrobishydrindone and truxene) which are produced from hydrindone itself (Kipping. *Trans.*, 1894, lxv., 480). Monobromohydrindone, unlike α-bromocamphor, is readily acted on by alcoholic potash, giving a condensation product of the composition $C_{18}H_{13}BrO_2$ (*Proc.*, 1895, x., 157). Dibromohydrindone resembles α-dibromocamphor in withstanding the action of nitric acid, but it differs from the camphor derivative in being readily acted on by alcoholic potash, giving a condensation product of the composition $C_{18}H_{11}BrO_2$; this substance crystallises from benzene in flat prisms, which contain 1 molecule of benzene, and melts at about 150°, also decomposing. A somewhat similar condensation product is obtained by treating dibromohydrindone with an alcoholic solution of sodium ethoxide; this compound crystallises in prisms melting and decomposing at 173—174°, and probably has the composition $C_{18}H_{10}O_2Br·OEt$.

Attempts to prepare hydrindene, $C_9H_{10}$, by first reducing hydrindoneoxime to the primary amine, $C_9H_9·NH_2$, and then converting the base into the hydrocarbon by the ordinary methods, were not more successful than those previously made by König (*Inaug. Diss.*, Leipzig, 1889), owing to the production of resinous compounds in the various stages of the process.

*Benzoylaminohydrindene*, $C_9H_9·NH·COPh$, prepared from the base, crystallises in colourless needles, and melts at 142—143°.

*Benzylideneaminohydrindene*, $C_9H_9·N:CHPh$, the condensation product of benzaldehyde and aminohydrindene, forms transparent prisms, melting at 74—75°.

*Aminohydrindeneoxalate* crystallises in clusters of white opaque prisms, and is rather sparingly soluble in cold methyl alcohol and in cold water.

*Hydrindone semicarbazide*, $C_9H_8:N·CO·NH·NH_2$, separates from dilute acetic acid in prisms, which contain 7 mols. of water; it melts and decomposes at about 239°.

*158. "Notes on Nitration."* By HENRY E. ARMSTRONG.

In previous notes on nitration (*Proc.*, 1891, vii., 87—91), E. C. Rossiter and the author have drawn attention to the part played by keto-compounds, and to the explanation which their formation, as well as that of other addition compounds, affords of the production of secondary products in nitrations.

Attention is now drawn to the conditions to be observed in preparing normal products of nitration. However carefully β-naphthol be subjected to the action of nitric acid, a considerable proportion of resin is always formed, even when the product is subjected to the action of reducing agents; but if bromo-β-naphthol be used instead, the formation of resin may be entirely avoided, a practically theoretical yield of 1 : 2-nitro-β-naphthol being obtained. Obviously, in the latter case, the addition compound which is first formed, and also the keto-compound derived from it, are far less sensitive to the action of the unchanged naphthol, so that the interaction affording the resin is prevented from occurring. Moreover, although a nitro-keto-compound, such as is represented by the formula—
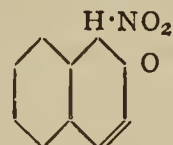


would not be converted by reduction into nitronaphthol, it is to be expected that if bromine occupied the place of the hydrogen, it would be readily removable. Not only is this actually the case, but nothing more powerful than a sulphite is needed; yet, in some instances, it is necessary to use a stronger reducing agent; thus, the compounds—
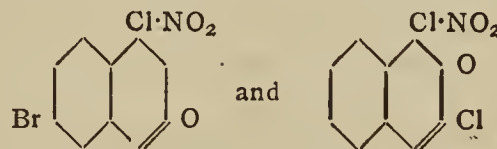


are unaffected by sulphite, but as experiments made by Mr. E. Rich show, they are at once converted into the corresponding nitronaphthols by means of hydrogen iodide.

*159. "3'-Bromo-β naphthol."* By HENRY E. ARMSTRONG and W. A. DAVIS.

At present, the only bromo-β-naphthol known is the 1 : 2-modification, which is the sole product of the direct interaction of bromine and the naphthol; indirect methods capable of affording isomeric forms are much needed. The authors have succeeded in devising a method of converting 1 : 3'-dibromo-β-naphthol into 3'-bromo-β-

naphthol by removing the bromine atom in position 1; this consists in digesting the dibromo-compound with a saturated solution of hydrogen iodide, ultimately at a temperature not exceeding 65°. If care be taken, the yield is that indicated by theory; but if the naphthol be allowed to dissolve in the acid solution, and the temperature to rise too high, an intractable condensation product is alone obtained.

3'-Bromo-β-naphthol crystallises from benzene in colourless needles melting at 127°; the acetate derived from it melts at 103°.

On sulphonation by means of cold sulphuric acid, it yields a somewhat unstable monosulphonic acid, which is converted into 1 : 3'-dibromo-β-naphthol by bromine, and into 1-nitro-3'-bromo-β-naphthol by nitric acid; doubtless, therefore, sulphonation takes place in position 1.

By heating the bromonaphthol with excess of sulphuric acid at 100°, a stable disulphonic acid is produced.

The behaviour of higher brominated derivatives of β-naphthol and of the bromo-α-naphthols with hydrogen iodide will be considered in a subsequent communication.

*160. "*Derivatives of Nitro-β-naphthols.*" By W. A. DAVIS.

The difficulties which attend the nitration of β-naphthol do not affect that of its ethers, which show no tendency to give keto-compounds; moreover, the nitromethoxy- and nitrethoxy-naphthalenes are all more or less intensely coloured substances, whereas the corresponding phenol derivatives are colourless; hence the investigation of these compounds is of importance from several points of view.

Besides repeating and confirming Gaess's observations on the nitration of β-ethoxynaphthalene (*J. pr. Chem.*, [2], 43), the author has prepared the methoxy-compounds corresponding to those described by Gaess, and has subjected both series to crystallographic examination. 1 : 2-Nitromethoxynaphthalene (m. p. 126°) is the main product when nitration is effected in acetic acid solution at a temperature not exceeding 15°; it forms 90 per cent of the total product, and is accompanied by about 1 per cent of the 1' : 2-nitromethoxy- (m. p. 69°) and about 3 per cent of the 3' : 2-nitromethoxy-compound (m. p. 134°).

The amido-derivatives were prepared by reducing the nitro-compounds with tin and hydrochloric acid. 1 : 2-Amidomethoxynaphthalene melts at 84°, and its acetyl derivative at 175°; the 3' : 2-amido-compound melts at 98°, and its acetyl derivative at 183°, whilst 1' : 2-acetamidomethoxynaphthalene melts at 145°.

The action of a molecular proportion of bromine on 1 : 2-nitroethoxynaphthalene gave 3' : 1 : 2-bromonitrethoxynaphthalene (m. p. 141°), the structure of which was determined by its formation on ethylating 3' : 1 : 2-bromonitronaphthol. When hydrolysed by alcoholic potash, it yields 3' : 1 : 2-bromonitronaphthol (m. p. 122°).

If any excess of bromine be used in the bromination, dibromethoxynaphthalene (m. p. 94°) and tribromethoxynaphthalene (m. p. 128°) are formed by the displacement of the NO₂ group by bromine.

3' : 1 : 2-Bromamidoethoxynaphthalene melts at 84°, and its acetyl derivative at 246°.

3' : 1 : 2-Bromonitromethoxynaphthalene, prepared by brominating 1 : 2-nitromethoxynaphthalene, melts at 152°; the corresponding amido-compound melts at 73°, and its acetyl derivative at 252°. 3' : 1 : 2-Bromonitronaphthylamine, obtained by heating 3' : 1 : 2-bromonitrethoxy- or methoxynaphthalene, with alcoholic ammonia at 160°, is a yellow, crystalline substance, melting at 190°.

On nitrating 1 : 2-nitromethoxynaphthalene with concentrated acid (*d* 1·42) at 0°, a mixture of 1 : 3' : 2 and 1 : 1' : 2-dinitromethoxynaphthalenes was obtained; these were separated only with difficulty. 1 : 3' : 2-Dinitromethoxynaphthalene was, however, obtained in a pure state by nitrating 1 : 3'-nitromethoxynaphthalene at 0°. It melts at 198°. The 1 : 1' : 2-dinitro-compound melting at

190° was obtained by similarly nitrating 1 : 1'-nitromethoxynaphthalene. The structure of these two dinitrocompounds was determined by converting them into the corresponding dinitronaphthylamines, which had been previously prepared and described by Gaess (*loc. cit.*).

1 : 2-Nitromethoxynaphthalene, on being heated with alcoholic potash, easily yields 1 : 2-nitronaphthol; on being heated with alcoholic ammonia at 160°, it is converted into 1 : 2-nitronaphthylamine. It is noteworthy that, under similar conditions, 1 : 2-nitronaphthol yields scarcely any nitronaphthylamine, a large amount of resin being formed.

SO₂Cl₂ is apparently without action on 1 : 2-nitrethoxy- or nitromethoxynaphthalene; it acts, however, very readily on 1 : 2-acetamidomethoxynaphthalene, giving a beautifully crystalline monochloro-derivative, melting at 167°. The structure of this has not yet been determined. In order to determine whether β-ethoxy-α-naphthylamine resembles β-naphthol or α-naphthylamine, the behaviour of its acetyl compound with bromine was studied; the action was carried out at 0°. 3' : 1 : 2-Bromacetamidoethoxynaphthalene, m. p. 245°, was obtained as sole product. Thus its behaviour is simply that of a derivative of β-naphthol in which position 1 is occupied, the NHAc group, apparently, being without influence; this is of especial interest, as, according to a private communication from Professor Nietzki to Professor Armstrong, its behaviour towards nitric acid is comparable with that of α-acetnaphthalide.

The behaviour of bromine with β-methoxy-α-acetnaphthalide is the same as towards the ethoxy-compound, 3' : 1 : 2-bromomethoxyacetnaphthalide (m. p. 252°) being obtained.

*161. "*Morphotropic Relations of β-Naphthol Derivatives.*" By W. A. DAVIS.

Although the crystallographic relationships of benzene derivatives have been very fully investigated, little work of a similar character has been hitherto carried out upon naphthalene compounds, and only one morphotropic series of derivatives has been recognised, viz., that afforded by the chloro- and bromo-naphthalenetetrachlorides, which has been discussed by Hintze (*Pogg. Ann.*, 1874, vi., 177). The author has examined the compounds referred to in the previous note, and finds the following crystallographic constants.

| Substance. | System. | Geometrical constants. $a : b : c$ |
| --- | --- | --- |
| 1 : 2-Nitronaphthol | Monosymmetric | 1·5755 : 1 : 1·1938 $\beta = 101° 26'$ |
| 1 : 2-Nitrethoxy-naphthalene | Orthorhombic | 2·4897 : 1 : 1·1606 |
| 1 : 2-Nitromethoxy-naphthalene | Anorthic | 0·9382 : 1 : 1·2088 $a = 97° 45', \beta = 92° 8', \gamma = 88° 27\frac{1}{2}'$ |
| 1 : 2-Nitrobenzyl-naphthol (Sayer) | Orthorhombic | 0·4892 : 1 : 1·0532 |
| 1 : 2-Acetamidomethoxynaphthalene | Monosymmetric | 0·7999 : 1 : 0·7611 $\beta = 99° 21'$ |
| 1 : 3' : 2-Nitrobromethoxynaphthalene | Anorthic | 1·4274 : 1 : 1·0265 $a = 95° 0', \beta = 109° 18', \gamma = 80° 15'$ |
| 1 : 3' : 2-Dinitromethoxynaphthalene | Orthorhombic | ? : 1 : 1·1526 |

The crystallographic data thus obtained afford a series presenting the following salient points :—

(1) In the transitions from 1 : 2-nitronaphthol to its methyl, ethyl, and benzyl ethers, although marked changes of symmetry occur, the axial ratio $c : b$ remains nearly constant. In the passage from nitro-β-naphthol (mono-

symmetric) to its methyl ether (anorthic), there is a degradation of symmetry; but an increase in symmetry occurs in passing from 1 : 2-nitronaphthol to its ethyl ether (orthorhombic). These changes of symmetry are analogous to those which occur in the benzene series in passing from acetanilide to methyl and ethyl acetanilide respectively, only in the latter case the changes are not brought into evidence by changes of system, but only by corresponding changes in the axial ratios.

(2) When 1 : 2-nitrethoxynaphthalene (orthorhombic) is changed by the introduction of a bromine atom into position 3', a degradation to anorthic symmetry takes place, the axial ratio $c : b$ remaining, however, nearly unaffected.

(3) A remarkable increase of symmetry occurs when 1 : 2-nitromethoxynaphthalene (anorthic) is converted into the 1 : 3' : 2-dinitromethylether (orthorhombic), whilst the ratio of the $c$ and $b$ axes remains nearly constant; this increase of symmetry accompanying the introduction of successive units of the same radicle is comparable with the change in symmetry that occurs in the benzene series in passing from paranitrophenol (monosymmetric) to di-nitro- and trinitro-phenol, both of which are orthorhombic, the symmetry in the case of the trinitro-compound tending towards that of the tetragonal system. When the various nitro-derivatives are melted on a microscope slide, and the solidified films are examined between crossed nicols, in the manner recently suggested by Mr. Pope (*Proc.*, 1896, xii., 142) the appearances they present are very characteristic, as the photographs which are exhibited show; and an important proof is thus given of the use to which such a method can be put either in identifying isomeric substances occurring together—particularly if these melt at nearly the same temperature and are, therefore, liable to be confused with one another—or in recognising the occurrence of a change from one crystalline modification to another.

*162. "*Researches on Tertiary Benzenoid Amines.*" II. By CLARE DE BRERETON EVANS, B.Sc.

In continuation of the experiments referred to in a previous abstract (*cf. Proc.*, 1896, xii., 235), the behaviour of diethylaniline, as well as that of dimethylortho- and dimethylpara-toluidine, has been further studied, and the series of isomeric dimethylanilinesulphonic acids has been completed by the preparation of the ortho-compound. For purposes of comparison, methyl- and ethyl-aniline have also been subjected to sulphonation.

Dimethylanilineorthosulphonic acid was prepared by methylating parabromanilineorthosulphonic acid and subsequently reducing the product.

The constitution of the acids derived from the toluidines was determined by methylating the sulphonic acids of toluidine of known constitution.

Summarising the facts, the striking conclusion has been established that whereas orthosulphonic acids are readily obtained from aniline derivatives—for example, parabromaniline, meta-acids only are formed from dimethyl- and diethyl-aniline and dimethylparatoluidine; there being, apparently, an extraordinary "aversion" on the part of the sulphonic radicle to take up the ortho-position relatively to the $NR'_2$ group.

A similar inhibiting influence apppears to be exercised by the group in preventing the entry of more than one bromine atom into the ortho-position. Such being the case, it is the more remarkable that when the sulphogroup does become displaced bromination extends much further in the case of the tertiary amines: dimethyl-aniline-para- and ortho-sulphonic acids being converted into *tetra*bromodimethylaniline and diethylaniline-parasulphonic acid even into *penta*bromodiethylaniline; 1 : 2 : 5-dimethylorthotoluidinemetasulphonic acid in like manner yields tetrabromodimethylorthotoluidine. Sulphanilic acid, it is well known, yields only *tri*bromaniline.

In the case of the acids derived from the dimethyltoluidines, viz.,—



I.    II.    III.
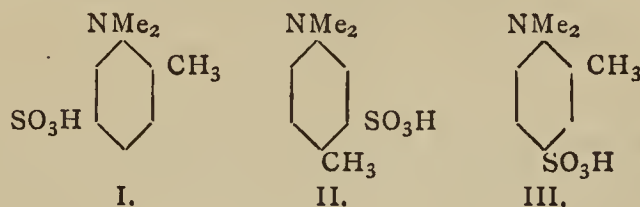
of which No. III. was prepared by methylating the toluidine sulphonic acid, only the first yields a perbromide.

It is noteworthy that the sulphochlorides of the various acids are all hydrolysed with somewhat unusual readiness.

Methyl- and ethyl-aniline are found to behave exactly as aniline, so that the presence of hydrogen in association with the nitrogen atom would appear to play a part in the formation of orthamido-derivatives.

It is proposed to extend the experiments to the dimethylxylidines and cumidines.

163. "*On the Circumstances which affect the Ratio of Solution of Zinc in Dilute Acids, with especial reference to the Influence of Dissolved Metallic Salts.*" By JOHN BALL, A.R.S.M.

The author considers the effects on the rate of solution of zinc in dilute acids of (i.) variations of concentration of the acid; (ii.) previous special treatment of the acid; (iii.) variations of temperature; (iv.) variations of pressure; (v.) variations of the surface condition of the zinc; (vi.) alloys of known amounts of foreign metals with the zinc; (vii.) performance of the solution in vessels of different materials; (viii.) addition to the acid solution of (a) oxidising agents; (b) reducing agents; (c) foreign acids; (d) salts of foreign metals.

The main portion of the paper deals with the effects produced by the presence of salts of various metals in the solution. Two main series of quantitative experiments for the comparison of the relative effects of salts of the different metals are described: one in solutions of sulphuric acid with magnesium, aluminium, chromium, manganese, iron. silver, copper, cobalt, or nickel sulphates as added salts; and one in solutions of hydrochloric acid, with manganese, lead, tin, copper, cobalt, gold, platinum, or nickel chlorides added. There is also a separate set of experiments in sulphuric acid solutions, with cobalt sulphate as added salt, in order to determine quantitatively the influence of the amount of salt used.

The metal used was pure distilled zinc, specially cast in very thin sheet. The results show that, both with sulphuric and hydrochloric acids, the addition of the foreign salts always accelerates the reaction, except in the case of magnesium and aluminium salts, which seem to be nearly without influence. The accelerating effect is most felt at the beginning of the reaction, and the velocity soon reaches a maximum (higher than that which would hold if no salt were present), which is practically constant nearly to the end. The acceleration is shown to be governed by a number of causes, of which the amount of metal precipitated from the added salt on the zinc is only a subordinate one, as the acceleration is often very great in cases where no precipitation can be determined—e.g., 0·020 grm. of nickel sulphate is added to a mixture of 17 c.c. of water, with 8 c.c. of sulphuric acid, at a temperature of 40°, increased the maximum velocity of reaction with zinc 37·87 times. In these cases a very minute trace of the added salt exerts an enormous influence, and, as shown by the experiments with cobalt sulphate, the effect of adding more of the salt becomes less perceptible as the total amount is increased, and ultimately we reach a point where further addition is without influence.

(To be continued).

## PHYSICAL SOCIETY.
*Ordinary Meeting, December 11th, 1896.*

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Prof. AYRTON, Vice-President, in the Chair.

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A PAPER on the " *Applications of Physics and Mathematics to Seismology* " was read by Dr. C. CHREE.

Prof. J. Milne has attempted to account for certain changes in the indications of spirit-levels and delicately suspended pendulums by the supposition that they are due to meteorological agencies, such as rainfall or evaporation. Thus he considers that a relative excess of moisture, say, on the west of an observatory, is equivalent to a surface load on that side, tending to make the ground on which the observatory rests slope downwards from east to west. The author, by making the assumptions as to the physical state of the substance of the earth, that it is a homogeneous, isotropic, elastic solid, has examined, in as general manner as possible, the amounts of flexure which would be produced by different systems of loading. He points out that the alteration in the reading of such an instrument as a spirit-level depends, not only on the bending of the surface of the earth, but also on the attraction exerted by the load, which slightly alters the direction of " gravity." He shows that if $\psi_1$ is the alteration in level produced by the bending, and $\psi_2$ the alteration in the direction of gravity, then the ratio $\psi_1/\psi_2$ depends only on the elastic constants of the earth, and is quite independent of the shape and size of the loaded area. In the case of a material having the elasticity of steel, $\psi_1/\psi_2 = 2$, for brass $\psi_1/\psi_2 = 5$, and for an incompressible material $\psi_1/\psi_2 = 11$. The author considers that this last value most truly represents what occurs in practice, and hence that the pressure effect is considerably larger than the gravitational effect. The pressure effect is worked out for the cases where the loaded area is a square, and a long narrow rectangle, and it is found that for a square of 100 metres side the effect, at a point 1 metre from one side, of loading the square with a layer of water 1 c.m. thick is to alter the level by 0·0012 seconds of arc. For the case of a tidal river 100 yards wide, and for a rise of 5 metres, the effect on an observatory at 100 yards from the bank would be to alter the level by 0·1 second of arc. Hence the effect of an estuary or tidal river is likely to be much more marked than differential evaporation or rainfall. The author also considers the effects of the attraction of the sun and moon, producing as they must " tides " in the solid crust of the earth, on the reading of a level, and the measured altitude of a star as obtained with an artificial horizon. Finally, the author considers the light the measurements on the velocity of propagation of earthquake disturbances throw on the credibility of the hypothesis he has made as to the elastic constants of the earth. He shows that the two observed velocities of 2·5 and 12·5 kilometres per second would lead to values for Young's modulus and the rigidity below those found in the case of iron; the bulk modulus, however, obtained is very high, and this he considers quite probable, on account of the enormous pressure to which the earth's deep-seated material is subjected.

Prof. PERRY said he had thought of taking up the subject from an experimental point of view, and trying the effect of loading a large block of indiarubber. He had not had time to refer to the author's paper, in which the reasons were given for taking the earth as incompressible. He (Prof. Perry), however, thought that this assumption led to results in contradiction to actual observed facts. Prof. Milne had obtained results which, for want of any other explanation, he had been compelled to attribute to meteorological causes. The reason Dr. Chree had obtained so small a value for the effect of loading by surface water might be because he had assumed erroneous values for the elastic constants. If he took a value for Poisson's ratio such as we meet with in practice, the effects would

be much larger. Prof. Darwin had also investigated the folding of the surface of the earth due to loading. The results obtained by the author with reference to the velocity of waves did not seem quite satisfactory. The small waves which were found, both at Berlin and the Isle of Wight, to precede the main waves coming from an earthquake in Japan, were not accounted for. The wave velocity, in an infinite mass of steel (a very elastic material) was about 6 kilometres per second, which was very different from 12·5 kilometres per sec. The author had assumed such values for the elasticity as would give the correct velocity.

The author, in reply, said that in applying the equations of elasticity to the earth's interior, unless the material were supposed nearly incompressible, one obtained values of the strains too large to be consistent with the fundamental mathematical hypothesis that the squares of strains are negligible. In the case of surface loading no such restriction was necessary, so far as the surface layers at least are concerned. The differences between the several numerical estimates for the ratio of gravitational and pressure effects of a surface load were principally due to the differences in the hypothetical values ascribed to the ridigity. It was his wish to make it clear that the pressure and gravitational agencies treated in detail in the paper were not the only ones likely to affect the level; he had specially called attention to solar heating and possible direct influence of moisture on the foundations of buildings, &c. The reason why for the one wave-velocity so much higher a value was obtained than that Prof. Perry calculated for steel was solely the high value, 24 : 1, found for the ratio of Thomson and Tait's elastic constants $m$ and $n$. He knew Prof. Darwin had treated of the phenomena met with in loose earth in some cases, but could not say whether this was what Prof. Perry referred to. He had himself once thought of attempting an application of what Prof. Karl Pearson termed the " equations of pulverulence," as treated in detail by Prof. Boussinesq, but had not done so, partly from a feeling of uncertainty as to their physical value. Supposing these equations satisfactory, they ought to give better results than the equations of elasticity when surface load was applied to a deep alluvial soil.

A paper on " *Musical Tubes*," by Mr. R. T. RUDD, was, in the absence of the author, read by the Secretary.

The author has examined a set of tubes ranging in length from 95 inches to 12 inches, made out of " 1-inch " gas-tube. Having tuned these to a diatonic scale, he found that there was a very marked difference in the character of the sound of the long, the middle, and the short tubes. Commencing with the long tubes, the first two octaves have a full rich tone, very similar to that of a church bell. They range from D of 145 vibrations per sec. to D of 580 vibrations. At about this point the tone changes from that of a church bell to one peculiar to tubes; the note also falls back in the scale more than a fifth, viz., to F♯ (360), the same tube giving two notes, to either of which the attention can be directed. In order to distinguish these different classes of sound produced by tubes, the author calls the tone corresponding to that of a church bell the " low grade," the next one the " middle grade," and that produced by short tubes (27 inches and under) the " high grade." At the junction between the high and middle grade there is a fall in the notes of about an octave and a half. The following formula may be used for calculating the pitch of the note given by a tube :—

$$V = \frac{D C}{L^2};$$

where V = frequency, D = external diameter, L = length, and C is a constant, which for iron tubes has the values $100 \times 10^4$, $62 \times 10^4$, or $22 \times 10^4$, according as the note belongs to the low, the middle, or the high grade.

·The author explains the effects by a consideration of the partial tones present and their effect on the ear.

Prof. RÜCKER said he thought it a great pity that in England such confusion of nomenclature existed, so that partials were often called overtones. He considered that the author had made an extremely ingenious attempt to explain the differences of pitch observed; this explanation apparently resembling that given by Prof. Everett to account for combination tones. The author explains the presence of a note of frequency 630 as being formed in the ear by the harmonics having frequencies of 1260, 1900, and 2600. He also explains the absence of lower partials having frequencies of 780, 390, and 140, by the supposition that they are so far removed from the "focus" as not to appreciably affect the ear. Another explanation of the presence of a note of frequency about 630 would, however, be the formation of a difference-tone between the partials of frequency 780 and 140.

Mr. BLAIKLEY agreed with Prof. Rücker as to the vagueness of the terms often employed, and said that it appeared that in the "high grade" the note was caused by the first proper tone in the "middle grade" by the second, and in the "low grade" by a difference-tone produced by the fourth, fifth, and sixth proper tones. The distance of the nodes from the end of the tube was 0·224 of the length and not 0·25, as the author states, and in the case of a tube clamped at the node this difference in the position of the clamp would have a marked effect on the tone. A great difference in the tone was also produced by varying the hardness of the hammer.

Prof. AYRTON said he had once investigated the behaviour of some tubes by analysing the note given out by means of a Helmholtz analyser. In the case of the tubes that gave a good note it was found that the components were few and well marked; while in that of the tubes which gave a bad note, the components were numerous and sometimes very ill-defined. The relative length, diameter, and thickness of the tube had a great influence on the tone.

The Society then adjourned till January 22, 1897.

## NOTICES OF BOOKS.

*Cycling as a Cause of Heart-Disease.* By GEORGE HERSCHELL, M.D. (Lond.). London: Baillière, Tindall, & Cox. 1896. Pp. 46.

To the best of our non-professional judgment the author makes out his case very well But is he, perhaps, not going too far to assert that a popular fad is almost certain to be physically or morally injurious?

Scientific Exploration in Balloons. — M. Mascart. —A number of captive balloons were sent up from different stations in the night between November 13th and 14th, and at the same time free balloons ascended from other stations. The free balloon sent off from Paris rose to the height of 15,000 metres, and recorded a temperature of −60°.—*Comptes Rendus.*

Determination of Nitric Acid in the Waters of the Seine, the Yonne, and the Marne, during the last Floods.—Th. Schlœsing.—The proportions of nitric acid carried down respectively by these three rivers in twenty-four hours were 351,000, 54,000, 107,000, and 486,000 kilos. It is remarked that the months of June, July, and August have been exceptionally rainy.—*Comptes Rendus.*

## CORRESPONDENCE.

### THE PROXIMATE CONSTITUENTS OF COAL.

*To the Editor of the Chemical News.*

SIR,—May I be permitted to add my protest to that of Messrs. Cross and Bevan (CHEMICAL NEWS, lxxiv., p. 294).

Not only is my note "On the Action of Dilute Nitric Acid on Coal" condensed into about twenty words,—of which perhaps I have no right to complain,—but it is preceded by an abstract ten times as long, taken from the note book of Mr. S. Shaw, a colleague of the Secretary to the Committee.

Of course I am the last person to protest against the superior value assigned to a research when made by a College lecturer, even when that value is 10 : 1, and it has not been published; but I do object to my results being misrepresented.

I am made to say that "a considerable portion of the coal is converted into a black insoluble acid."

Now my note contains the following:—

"The insoluble matter from 90 grms. of coal was found to be 12·5 grms. consisting of coarse particles of coal-sand, &c.

"One grm. of coal, ground in an agate mortar and similarly treated, left only a trace of insoluble matter, so that in some varieties of coal the whole of the organic matter of the coal undergoes change." (*Proc. Chem. Soc.,* viii., 10, Feb. 1, 1892).

After this one is not surprised to find that Mr. Shaw's method, which it is suggested by the space, position, and date assigned to it, anticipated mine, consisted in treatment for three weeks with nitro-sulphhuric acid, and that a "considerable proportion" thus became soluble in caustic alkali, whilst my process consisted in treatment with 49 per cent nitric acid, for six hours, the temperature being gradually raised toward the end of the time to 100°, and that thus the whole of the coal became soluble in dilute carbonated alkali.

I have since pushed these researches much further, on a large scale and on many coals, and hope some day to publish more complete results.—I am, &c.

R. J. FRISWELL.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences.* Vol. cxxiii., No. 21, November 23, 1896.

Michel Lévy was elected a member of the Mineralogical Section of the Academy of Sciences *vice* the late M. Daubrée.

Various Properties of the Uranic Rays.—Henri Becquerel.—This paper will be inserted in full.

Discharges of the Röntgen Rays; Influence of Pressure and Temperature.—Jean Perrin.—At a constant temperature, and for one and the same gas, the quantity of electricity dissociated per unit of mass is independent of the pressure and proportional to the absolute temperature.

Illusions which accompany the Formation of Penumbræ. Applications to the X Rays. — G. Sagnac.—This paper requires the three accompanying figures.

**Action of certain Hydrogen Compounds upon Thionyl Chloride.**—A. Besson.—Not suitable for abstraction.

**Crystalline Neutral Magnesium Chromite.**—Em. Dufau.—At the elevated temperatures produced by the electric arc chromium sesquioxide combines directly with magnesia, without any intermediate agent, yielding neutral chromite, $Cr_2O_4Mg$, in octahedral crystals. Whatever the intensity of the arc employed we obtain nothing comparable to the calcium or the barium compounds, $Cr_2O_3.4CaO$, or $4Cr_2O_3BaO$, the neutral compound being always obtained.

**Salts of Hexamethyleneamine.**—M. Delépine.—A thermo-chemical paper. Hexamethyleneamine is a very feeble base.

**Rôle of Boric Acid in Glasses and Enamels.**—L. Grenet.—An excess of base occasions denitrification; that is, the crystallisation of definite borates and silicates. An excess of boric acid separates the glass in the bath into two layers, the upper being boric acid almost pure, and the lower glass saturated with boric acid.

**Detection of Caramel in Wines. Possible Confusion with the Coal-tar Colours.**—A. J. de Cruz Magalhaès.—This paper will be inserted in full.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Parts 4 and 5.

**Determination of Saccharin in presence of Salicylic Acid.**—Haers proposes (*Wochenschrift f. Brauerei*) to eliminate the latter by conversion into sparingly soluble dibromsalicylic acid.

**Examination of Tanning Materials.**—Notices of a number of papers by Jocum (*Leather Manufacturer*), Weiss (*Der Gerber*), Cezch (*Der Gerber*), Schrœder and Bartel (*Dingler's Polytech. Journ.*), H. Krug (*Journ. Am. Chem. Soc.*).

**Determination of Starch in Cereals, Potatoes, and Commercial Starches.**—A series of papers by R. Sachsse and R. H. Chittenden (*Journ. of Analyt. Chem.*), Bauer (*Chemiker Zeitung*), H. Ost (*Chemiker Zeitung*), P. Guichard (*Journ. der Pharmacie*), Soxhlet (*Wochensch. fur Brauerei*), L. Sartagni (*Studi e ricerche del Lab. di Chimica agraria di Pisa*), Lintner and Dull (*Zeit. Angew. Chemie*), Munsche (*Chemiker Zeitung*), Winton (*Journal Anal. Chemistry*), Reinke (*Dingler's Polyt. Journal*), Schreib (*Zeit. Angew. Chemie*), Berger (*Chemiker Zeit.*), J. Krieger (*Chemiker Zeit.*), Asboth (*Repert. Anal. Chemie*), Lintner (*Zeit. Angew. Chemie*), Leclerc (*Journ. der Pharm.* and *Chemiker Zeitung*), &c.

**Table of Corrections for the Klosterneuburg Must Glass.**—Drawn up by H. Pfeiffer (*Weinlaube*).

**Spanish Earth for Clarifying Wines.**—J. Nessler.—(*Weinlaube*).

**Detection of Dulcin in Beverages.**—A. Jorissen (*Journal de Pharmacie de Liége*) uses a solution of mercury nitrate free from any excess of acid. Dulcin, insulated according to Morpurge's process, is suspended in 5 c.c. of water, and heated with 2 to 4 drops of the reagent in a boiling water-bath for five to ten minutes, when, if dulcin is present, the liquid takes a violet-blue colour.

**Colour Reactions of Saffron and its Adulterants.**—A. Tschirch and O. Oesterle.—A tabular conspectus.

**Chicory in Belgium.**—Only the root of wild chicory may be used in groceries.

**Volumetric Determination of Iron in the Ash of Plants and Animals.**—M. Ripper (*Chemiker Zeitung*).—An iodometric process.

**Detection of Small Quantities of Hydrogen Peroxide in Organic Fluids.**—A. Richardson.—From the *Journal of the Chemical Society.*

**Determination of Alumina in the Ash of Plants.**—M. Berthelot and G. André.—From the *Comptes Rendus.*

# THE CHEMICAL NEWS.

## VOL. LXXIV., No. 1935.

## THE PROGRESS OF SPECTROSCOPY.

### By H. KAYSER.

As I here, for the first time, give a survey of the development of spectrum analysis, I may be permitted not merely to keep the past year in view, but to reach further in order to render the sequel more intelligible. Whilst the discoverers of spectral analysis—as the very name implies—thought of qualitative analysis, this application has scarcely held good; there are only a few elements for which chemists utilise the spectroscope in this direction. The enormous enthusiasm with which the discovery of Kirchhoff and Bunsen was received disappeared, therefore, with relative rapidity. The interest in spectroscopy was revivified in 1867 by the discovery of the gaseous nature of the protuberances, the lines of which showed further displacements from their correct positions, and thus by the application of Doppler's principle, led to determinations of velocity. Lockyer especially worked energetically; he undertook a re-determination of the spectra of the elements, but failed in this enterprise, which led him to the hypothesis that all the elements were compounded of ingredients which are common to many of them.

Although spectroscopic work never came quite to a stand, there elapsed a decennium before a real new impulse can be signalised, which still continues and daily bears new important fruits. The main cause of this impulse may be sought in two circumstances: the construction of Rowland's gratings, especially the concave gratings, and the following applications of photography. Gratings existed since the beginning of the century, when they were introduced by Fraunhofer, but they were much too small, and therefore feebly illuminating, too inaccurately divided, and, finally, much too expensive to compete with prism apparatus. But, on the one hand, prisms were used, and on the other the visible part of the spectrum, which was best known by ocular inspection, could not be photographed until H. W. Vogel had rendered his principle of optical sensitiveness practically available by the invention of the plates sensible to colours (1884). The old spectrum analysis had been wrecked on the circumstance that the spectra of the several chemical elements could not be determined with sufficient accuracy and completeness. We had scarcely advanced so far as to determine in the visible part the wave-lengths of the main lines to an Ångström unit (A. U. = 1 ten-millionth m.m.). But as often a dozen lines of different elements fall within an A. U., it was found impossible to ascertain the chemical constituents of a substance from its spectral lines. The first condition for a faithful development was, consequently, a more accurate determination of the spectra of the elements. This task was undertaken since 1878 by Liveing and Dewar, who, for the first time, obtained a true insight into the ultra violet spectra of some elements, whereby they evaporated the substance in the electric arc. Hartley and Adeney carried out similar measurements for the spark spectra. But excellent as were these determinations in comparison with those of an earlier date, they were insufficient, as they were not executed with Rowland's gratings; hence the dispersion did not suffice to attain the accuracy required. In most cases we may indicate a line as known when its wave-length is certain as far as 0·1 A. U., but after all this does not suffice, and for modern spectrum measurements we must consider 0·01 the limit of accuracy to be aimed at. This, however, can be attained only by such great dispersions as

Rowland's gratings admit of, and hence Rowland was the first to publish measurements in which the $\frac{1}{1000}$ of an A. U. was given. They referred to the solar spectrum, and appeared with the splendid atlas of the solar spectrum which Rowland obtained in a purely photographic manner, and published in 1889. A systematic measurement of the spectra of the elements, photographed by means of Rowland's concave grating, and in which an accuracy of at least some hundredths of an A. U. was attained, was undertaken in 1887 by Kayser and Runge. Hitherto only the arc spectra of the alkalis, the alkaline earths, of Fe, Cu, Au, Ag, Zn, Cd, Hg, Al, Ir, Tl, As, Pb, Bi, Sn, Sb, have appeared, but other elements are to follow. More accurate measurements of limited parts of some spectra have also been published by Hasselberg and Rowland.

With the aid of such measurements it will now be possible to effect trustworthy qualitative analyses; though it must be admitted that the need for such will rarely occur. Spectral analysis is mostly too delicate for general chemical uses; it shows everywhere traces of impurities which are chemically far from distinguishable and of no significance. But in many cases, *e.g.*, in the determination of the atomic weights of the elements, the chemist ought to ascertain the purity of his substances spectroscopically.

A comparison of the solar spectrum with the spectra of the elements was effected by Rowland (1891), and led him to the result that there are present in the sun: Fe, Ni, Ti, Mn, Cr, Ca, C, Va, Mo, Pd, Mg, Na, Si, Zr, Ce, Ca, Sc, Nd, La, Y, Nb, Er, Zn, Cu, Be, Ge, Sr, Ba, Al, Cd, R, Sn, Pb, K. Not present are: Sb, As, Bi, B, Ni, Cs, Au, In, Hg, P, Rb, Se, S, Tl, Pr. The other elements are doubtful or not yet examined. In the last year Rowland has begun to publish a list of the wave-lengths of all the refrangible lines.

Probably the most important advance has been rendered possible by the more accurate measurement of the wave-lengths. As far back as thirty years ago, we had begun to search for relations between the wave-lengths of the lines of one and the same element, as also between the lines of different elements. As we assume the vibrations of the ether corresponding to the different lines are directly excited by the vibrations of the atoms, as, moreover, the vibrations of a body depend on its mass, and on the forces acting upon it, so that as soon as these are given all the vibrations which the body can execute are firmly determined. We must expect that all the lines of an element are in regular connection, and may be included under a mathematical equation exactly as the different possible vibratory numbers of a string, an organ pipe, a bell, &c., can or might be regenerated by a formula. As the constants of such a formula depend on the mass of the energies of the atoms, *i.e.*, on the same magnitudes which determine the chemical nature; as, further, in bodies chemically akin these magnitudes will be similar, it was to be expected that relations will be found between the spectra of bodies chemically allied to each other, and that such bodies would appear to be—so to speak—built on the same plan. Balmer first observed that the lines of the simplest spectrum known—that of hydrogen—can be represented by the equation—

$$\lambda = A \, \frac{n^2}{n^2 - 4} \, ;$$

where we then insert for $n$ the numbers from 3 to 15, and A is a constant, 3647. All the lines are thus combined in a series. Kayser and Runge succeeded in showing that in the spectra of several elements there exist such series, which may be represented by the equation—

$$\frac{1}{\lambda} = A + \frac{B}{n^2} + \frac{C}{n^4} \, ;$$

inserting for $n$ the series of whole numbers from 3 upwards, and for A, B, C different values which vary from element to element. The spectra of the alkalis appeared

built alike; they consist of three series of pairs of lines. In one of the series, comprising the strongest ines of the spectrum, the two lines of each pair move closer together as we approach the shorter wave-lengths. This series is called the chief series, in the others are the accessory series; in the latter the difference of vibration, *i.e.*, the difference of the number of vibrations of both lines remaing identical for all the pairs. In each series the brightness of the lines declines regularly with the increasing *n*, *i.e.*, the more we approach the ultra-violet. The two accessory series terminate at the same point of the spectrum. In Cu and Ag the same accessory series of pairs have also been found. In the spectrum of Mg, Ca, Sr the two series have also been shown, but they here consist not of pairs, but of triplets, arranged so that the difference of vibrations of the first lines is about twice as great as that between the second and third line. The same holds good for the groups Zn, Cd, Hg. In the groups Al, In, Tl finally the two series of pairs occur.

So far as the investigations have been hitherto extended, we may, therefore, by analogy of the spectra, distinguish the following groups:—1. Li, Na, K, Rb, Cs; 2. Cu, Ag; 3. Mg, Ca, Sr; 4. Zn, Cd, Hg; 5. Al, In, Tl. In each group the difference of vibrations of the pairs or of the two triplets increases with the atomic weight of the elements, and it is about proportional to the square of the atomic weight. In each group, with the increasing atomic weight, the spectrum advances continually to long wavelengths, as if the heavy atoms vibrate more slowly. From group to group there occurs a considerable displacement of the spectrum towards the ultra-violet. For instance, the accessory series for Li end at 3498 A. U.; for Na at 4069; for K at 4545; for Rb at 4776; for Cs at 5065. On the other hand, this end is displaced from Li 3498 to Cu 3165, to Mg 2514, to Kn 2328, to Al 2070. Hence follows the unpleasant result that for further groups of elements which belong together we have to seek the series among still smaller wave-lengths which cannot yet be photographed. Rydberg has arrived independently at similar results to those of Kayser and Runge, but he has sometimes arrived at untrustworthy conclusions by the use of old measurements.

A foremost and highly interesting application of these researches must be mentioned among the literature of last year: the work of Runge and Paschen on the gas evolved from clèveite.

In 1868 Lockyer discovered in the extreme cooling of the solar surface the so-called chromosphere, a very bright yellow line which does not occur as a dark line among the Frauenhofer lines, and had not been recognised in any terrestrial element. It was called the line $D_3$, and the hypothetical element from which it was produced was known as helium.

In the present year Ramsay discovered that the gas escaping from clèveite on heating or on boiling with sulphuric acid did not consist of pure nitrogen, as had been previously assumed, but contained at the same time a gas which remains after removal of the nitrogen, and is chemically quite indifferent. This gas showed in Geissler tubes the line $D_3$ in extreme strength, along with a great number of other lines. The existence of an element which had been assumed for twenty-seven years, on the evidence of a spectroscopic observation, was thus demonstrated. But did the clèveite gas consist of helium alone or were we in presence of a mixture of several new elements? The latter view was indicated by the experiments of Lockyer, in which certain lines appeared of a variable intensity. Runge and Paschen measured the spectrum photographically with a Rowland's grating, and found that its lines could be arranged in six series, three of which consist of narrow double lines. Of these, two possess constant differences of vibration and terminate at the same place; the third, which contains the strongest lines, contains couples of a decreasing difference of vibration. The three series thus form conjointly a spectrum which exactly corresponds to the type of the alkalis; these are the two

by-series, and the main series. The three remaining series of the clèveite gas display simple lines; the two fainter run out at the same place, and are therefore two by-series; the third is the main series. Runge and Paschen thus draw from their experiments the certain conclusion that the clèveite gas consists of two elements, and two only, as all the lines found are included by the six series. The first element is helium, the second has not yet received a name. The different position of the series further permits us to infer that helium has a higher molecular weight than the anonymous gas. The lines of both elements have long ago been observed in the chromosphere and in many stars. In the chromosphere the helium lines are decidedly stronger than those of the other gas. In many stars this is reversed, so that we find here a differentiation of the two elements in nature. This very careful investigation of Runge and Paschen's shows most plainly the importance of the series.

The third element, also discovered in the last years, argon, which Rayleigh and Ramsay succeeded in demonstrating in 1894 as a constituent of the earth's atmosphere, is hitherto characterised alone by its spectrum. According to the strength of the discharge passed through Geissler tubes filled with argon, it glows with a red or a blue light, and thus displays two quite distinct spectra, which were first photographed and measured by Crookes. Both spectra are as yet very imperfectly known. According to my own investigations, not yet quite completed, both spectra have not a single line in common. Whether argon is a new element, or a mixture, or—as some suppose—only a modification of nitrogen, can be decided only after a more thorough measurement of its spectrum. Hitherto I incline to the view that we have to do here with only a single new element. In many mineral springs there rise up bubbles of gas, which were formerly considered as nitrogen. I first observed that the gas from the Wildbad springs, along with nitrogen, contains considerable quantities of argon and helium. The same result has since been ascertained in various other springs. I have also detected the presence of helium in atmospheric air, that at least of Bonn.

Of the other spectroscopic literature of the last years, an entire series of researches by Eder and Valenta require especial notice. Thus the spectrum of the spark of carbon has been examined in all possible conditions, the absorption by different kinds of glass, and other bodies optically important; the ultra-violet spectrum of the flame reactions and other phenomena have been investigated. In mercury the authors found a band spectrum hitherto unknown; interesting because mercury forms a so-called monatomic gas, whence the possibility of various spectra would seem to many improbable.

In its astronomical applications spectroscopy has to record decisive results, though I must here confine myself to brief indications. In the nebulæ it was formerly believed that hydrogen and nitrogen had been recognised; but Keeler has shown by his classical measurements that nitrogen is not present. On the other hand, numerous nebular lines have been photographically registered, mostly of unknown origin. The spectra of many stars have been of late photographed with much greater accuracy than it was formerly possible. Still, the results are far from being sufficient to unfold the chemical composition of the stars. The principle of Doppler has met with important applications. It shows that if a luminous body approaches us or recedes from us with the rapidity *u*, the lines in its spectrum are displaced towards the blue or the red, so that, instead of the true wave-length λ, there appears another, $λ_1$, where—

$$\lambda_1 = \lambda \left( 1 + \frac{u}{v} \right);$$

where *v* indicates the rapidity of light. From an observed change of the wave-length, *e.g.*, of the hydrogen lines, we may therefore calculate the velocity of a star towards us or away from us " in the radius of vision."

Such measurements have been very much improved by the introduction of photography, and they have been latterly carried out by different observers. In the same manner Keeler has been able to show that the ring of Saturn is no solid body, but consists of a number of small discrete parts—meteors. As the ring rotates, one side approaches us, whilst the other side recedes from us ; the rays coming from the former side appear displaced towards the blue, and those from the latter side towards the red. Keeler observed that on the inside of the ring the displacement is greater than that on the outside ; whence it follows that the ring is no continuous solid body.—*Chemiker Zeitung.*

## DETERMINATION OF ALUMINA IN PHOSPHATES.

### By HENRI LASNE.

THE determination of alumina in phosphates presents not merely a scientific interest, but a great commercial and industrial importance. We know, in fact, that the presence of sesquioxides is very detrimental to the manufacture of superphosphate.

If iron can be easily determined by means of standard solutions, the separation of alumina is difficult, and the methods proposed for this purpose fail, either from an inadmissible inaccuracy or from the great difficulty of their execution.

*Solution of the Phosphate.* — I prefer to treat with hydrochloric acid, evaporating to dryness in presence of the insoluble matter. The fluorides are completely decomposed, and the silica is rendered insoluble ; these two conditions are indispensable, as the silica and the silico-fluorides would accompany the alumina in its reactions.

To facilitate the execution of the procedure described below, it is well to re-dissolve in the smallest possible quantity of hydrochloric acid,—say 1 to 5 c.c. per grm. of phosphate,—to dilute with 20 vols. of water, and to heat. After thirty minutes the solution is filtered, and the filtrate is ready for the determination of the alumina.

In all the methods hitherto proposed the two sesquioxides are precipitated together, either in the free state or as phosphates. The precipitate is weighed and re-dissolved, the iron being thus determined volumetrically and the alumina found by calculation. This method would certainly be legitimate if we were sure of obtaining all the alumina and of knowing the exact composition of the precipitate obtained,

The separation of the phosphoric acid involves long and troublesome operations if we wish to obtain complete accuracy. Molybdic acid especially can only be separated from the sesquioxides by means of sulphuretted hydrogen.

The methods in which the sesquioxides are weighed in the state of phosphates fail as regards the base, as we do not know the composition of the precipitate obtained, which is very variable, as the following study shows :—

*Precipitation of the Alumina in the state of Phosphate.* —Two points have to be examined, the solubility of the precipitate and its composition.

In an acetic liquor aluminium phosphate is soluble enough to involve considerable losses, and to cause this method of precipitation or separation to be rejected irrevocably. The solubility diminishes on boiling.

In a solution very scarcely ammoniacal in presence of ammonium chloride the solubility is null, and the precipitation is entire.

I call attention to a method of precipitation which has not yet been applied. Ebullition for half an hour with ammonium hyposulphite suffices for complete precipitation (in place of three hours for pure alumina). The precipitate is easy to filter and wash : it is granular, like that of alumina in the Chancel process. The solubility is so light that the greatest care is required for its detection.

The composition of the precipitate varies with the method, the degree of acidity of the liquid, and the excess of phosphoric acid which it contains, and that progressively.

The quantity of phosphoric acid combined with one and the same quantity of alumina is minimal in a slightly ammoniacal solution in which the neutral phosphate is partly dissociated, even when the liquid contains fifteen times more phosphoric acid than is necessary. In an acetic liquid, on the contrary, and especially in ebullition, the composition of the neutral phosphate is exceeded, even in presence of a very slight excess of phosphoric acid.

If we examine more closely the precipitation of ammonium hyposulphite, we see that the proportion of phosphoric acid in the precipitate does not regularly follow the excess contained in the liquor in which it is formed. If, on setting out from a liquid containing the elements of a neutral aluminium phosphate, we add increasing doses of ammonium phosphate, the proportion of phosphoric acid in the precipitate, at first below that corresponding to neutral phosphate, goes on increasing very rapidly up to a proportion representing an excess of 0·5 grm. phosphoric acid per litre ; *between 0·6 grm. and 1 grm. it remains stationary, and corresponds exactly to the neutral phosphate ;* beyond this point it is increased anew.

We obtain, therefore, the neutral phosphate exactly if we effect the precipitation in a liquid containing per litre 0·8 grm. of phosphoric acid in the state of ammonium phosphate, and this condition presents an elasticity sufficient to be easily realised.

When the liquid contains alkalis the aluminium phosphate carries down a certain proportion of these substances, forming a kind of lake.

The precipitate must be ignited before the blast for fifteen minutes, to lose entirely its water of combination.

*New Method for the Separation of Aluminium.* — Soda dissolves alumina in presence of an excess of phosphoric acid ; all the bases which usually accompany it—*i. e.,* lime, magnesia, iron, manganese—are entirely precipitated either as phosphates or as sesquioxides. In order that the separation may be complete the phosphoric acid must be in excess, otherwise there is formed a calcium aluminate insoluble in soda. If this condition is maintained not a trace of alumina remains in the precipitate. To be certain of this some precautions must be taken during the washing, to avoid the soda from becoming carbonated.

When the solution of alumina is obtained, two successive precipitations are necessary, since the second only enables us to obtain a pure compound of known composition.

For instance, for 1·25 grms. of phosphate, in a solution free from silica and slightly acid, we dissolve, in a capsule of nickel, 5 grms. of caustic soda *free from silica and alumina,* and 1 grm. of sodium phosphate. Into this we pour the solution or phosphate, stirring and keeping it at 100° for one hour. We make up to 250 c.c., and to take account of the volume of the precipitate we add, as a correction, 0·5 c.c. of water. We take 200 c.c. of the filtrate, continuing the operation with 1 grm., and thus avoiding any inconvenience from carbonation during washing.

The first precipitation is effected by acidulating, adding ammonium chloride, and then ammonia in very slight excess. The gelatinous precipitate would be difficult to wash, but this is needless. It is sufficient to drain it ; it is then easily re-dissolved in hydrochloric acid, diluted to $\frac{1}{20}$, and heated.

To the solution thus obtained we add 3·5 c.c. of a 10 per cent solution of pure ammonium phosphate, to neutralise with ammonia without going as far as the production of a permanent precipitate, diluting to about ¼ litre, and adding 1·5 grms. ammonium hyposulphite. It is

boiled for half an hour, keeping the volume constant, then adding 5 drops of ammonium acetate in a saturated solution, and continuing the ebullition for ten minutes. It is filtered, and washed completely with hot water. It is ignited before the blast for fifteen minutes. The weight of the precipitate multiplied by 0·418 gives the weight of the alumina. We then add 0·8 m.grm. to take account of the slight solubility detected.—*Comptes Rendus*, cxxi., p. 63.

## AN ELECTROLYTIC METHOD FOR THE DETERMINATION OF MERCURY IN CINNABAR.*

### By W. B. RISING and VICTOR LENHER.

WHEN a rapid solution of cinnabar is desired, heretofore, oxidation with aqua regia has seemed most convenient; the length of time required to expel the nitric acid used, and the likelihood of loss of mercury by distillation in hydrochloric acid, are serious hindrances to the use of this method. Hydrobromic acid dissolves very readily mercuric sulphide, as well as many other naturally occurring sulphides with the evolution of hydrogen sulphide and the formation of the bromide.

If this solution be nearly neutralised with caustic potash, pure potassium cyanide added in sufficient excess to dissolve the cyanide first precipitated (Smith, "Electro-Chemical Analysis," p. 58), and electrolysed with a weak current, the mercury will be readily deposited as metal on a platinum dish used as a negative electrode. The use of hydrobromic acid is to be recommended, as it gives such a ready method of decomposition, and can be used at low temperatures, when there will be no loss of mercury by distillation.

The hydrobromic acid used in the following experiments was prepared by treating potassium bromide with sulphuric acid of 56° Baumé; the gas was conducted into water, as in the preparation of hydrochloric acid. By using potassium bromide with the above strength of acid, hydrobromic acid quite free from bromine can be readily prepared.

The ordinary hydrobromic acid used in the laboratory, containing bromine, could be used in the following experiments:—

The first sample which was worked with was pure mercuric sulphide. Hydrobromic acid of constant boiling-point—*i. e.*, 49 per cent—was diluted with water 1 to 4, and the sample treated with as little excess as possible over what would be necessary for its solution; the slight excess of acid was neutralised with potassium hydroxide, potassium cyanide added in excess, and the solution electrolysed by a current giving 0·025 ampères N.D.$_{100}$.

The following results were obtained:—

| Mercuric sulphide. Grm. | Mercury found. Grm. | Mercury per cent. |
|---|---|---|
| 0·2110 | 0·1818 | 86·16 |
| 0·2058 | 0·1774 | 86·20 |

The second sample was a naturally occurring cinnabar; determination *a* was made, using the decomposition by aqua regia, evaporating off the excess of nitric acid with hydrochloric, neutralising the excess of hydrochloric acid with potassium hydroxide, adding potassium cyanide in excess, and electrolysing as before: *b* and *c* were treated with 20 per cent hydrobromic acid at the boiling temperature; solution was effected in a few minutes, the excess of acid was neutralised by potassium hydroxide, potassium cyanide added in excess, and electrolysed with the same strength of current as before.

Results were:—

| | Cinnabar. Grm. | Mercury found. Grm. | Mercury per cent. |
|---|---|---|---|
| *a* | 0·2024 | 0·1046 | 51·68 |
| *b* | 0·2514 | 0·1299 | 51·67 |
| *c* | 0·5135 | 0·2656 | 51·72 |

The last sample was a lower grade cinnabar, very silicious, and long digestion with either hydrobromic acid or aqua regia was necessary. In this last experiment the action of the hydrobromic acid was very much more rapid than that with aqua regia. The mercury was deposited from a cyanide solution as before.

Results were, using hydrobromic acid as solvent :—

| | Cinnabar. Grm. | Mercury found. Grm. |
|---|---|---|
| *a* | 0·2011 | 0·0616 |
| *b* | 0·2011 | 0·0622 |

Using aqua regia as solvent :—

| | Grm. | Grm. |
|---|---|---|
| *a* | 0·2030 | 0·0629 |
| *b* | 0·2030 | 0·0631 |

## THE OXIDATION OF SILVER.

### By CHARLES E. WAIT.

IN a former paper (*Trans. Am. Inst. Min. Eng.*, xv.) I had occasion to call attention to the large amount of silver present in a sample of bismuth litharge from a western smelting and refining company. The silver in this instance, estimated in the metallic state, was 2·94 per cent.

There was some doubt expressed as to the condition in which the silver existed, it being usually reported in the metallic state. Upon investigation it was found, as was shown in the paper referred to, that the silver did not exist wholly in the metallic state, but partly in another form, probably the oxide.

The conclusions reached at that time were based upon the following experiments :—

1. A weighed sample of the litharge was boiled in acetic acid for about half an hour, the solution was filtered, and the filtrate gave no reaction for silver.

2. Same as above, but with continued boiling; the filtrate gave no reaction for silver.

3. A sample was placed in cold acetic acid, kept there for half an hour, then heated to boiling; the solution was filtered, the lead was precipitated, and in the filtrate silver was found to exist, corresponding to 19·25 per cent of the silver in the litharge. Other determinations gave closely agreeing results, and it is interesting to note that the residues contained grains of metallic lead or argentiferous lead.

I have placed the following interpretations upon the above results :—

In Nos. 1 and 2 if any silver in any form was dissolved in the acetic acid, it was in turn re-precipitated by boiling in the presence of metallic lead.

In No. 3 the silver dissolved did not in all probability exist in the metallic state; and in this case was not precipitated by the lead, or argentiferous lead, the solution being brought merely to the boiling temperature.

I have been led to the above interpretations by showing that neither metallic silver reduced to fine subdivision by mechanical means, nor silver freshly prepared by zinc from silver chloride, is soluble in acetic acid, while argentic oxide is soluble in that acid; and a solution of silver oxide in acetic acid was precipitated completely by metallic lead upon boiling.

If the oxides are decomposed at a temperature of 300° C. (Roscoe and Schorlemmer, vol. ii., Part 1), or less (*Journ. Chem. Soc.*, lxv., 316), how may we account for

the existence of this substance in a product so highly heated as the litharge from the refining furnace?

Berthier (Crookes and Röhrig, " Metallurgy ") has observed that lead may be oxidised by oxide of copper, when melted together, and further consideration of the subject shows that certain metals may be oxidised by being melted with an oxide of another metal, this oxidation depending in all probability upon the excess of the oxide present. Silver does not appear to be oxidised by oxide of copper if the results in experiment No. 18 are trustworthy.

According to Fournet's experiments (*Erdman's Journal*), silver is not an exception to the metals to which litharge gives up a part of its oxygen when fused with them for a considerable time.

While it is true that in the process of cupellation there is a loss of silver due possibly to oxidation, yet I do not find any losses even in the most exaggerated cases at all comparable with the percentages of silver oxide which I have been able to produce by a simple, yet possibly new, method.

It seemed to me an interesting problem to ascertain, if possible, the conditions under which silver may be oxidised at a high temperature, and the conditions under which the oxide of silver, if thus formed, would remain as such.

Some interesting work has been done along a similar line (*Journ. Chem. Soc.*, April, 1894); that is, a study of those oxides which are stable at high temperature, and those which are decomposed, but under neither head does silver seem to have been discussed.

So few observations have been made along this exact line, as far as I have seen, that I have been induced to make some investigations with a view to throw light upon the subject, if possible.

The general method of conducting the experiments, I will briefly state as follows :—Metallic silver in minute subdivision was incorporated with one of the several bodies mentioned below; this mixture was put in a cupel of bone-ash, or in a scorifier, and then placed in the muffle of an assay furnace and subjected to an oxidising heat.

After this operation the mass was removed to a mortar, pulverised, then digested with acetic acid to boiling, the solution was filtered; in case a lead compound had been used, the lead was removed by sulphuric acid, hydrochloric acid was then added. The silver chloride thus formed was filtered, dried, and wrapped in least pure lead foil, and then carefully cupelled.

There was thus obtained the silver, which was converted to argentic oxide—at least I assume it to be such—and it is interesting to note that the amount of silver converted to oxide, and tabulated below, shows a very great range—in fact, from only a trace to as much as 39 per cent of the silver used.

This variation seems dependent upon a number of conditions, namely, the body with which the silver was mixed, duration and condition of heat, whether low, medium, or high temperature. As I did not use a pyrometer to ascertain the temperature during these experiments, I have thought it desirable to indicate the degree of heat approximately by such terms as " low," " medium," and " high," referring to the condition of the heat as usually obtained in the muffle in the assay of silver.

I append herewith several tables of experiments and results :—

TABLE A.

| No. of expt. | Ag in grms. | Heated with— Grms. | Time of heat. Minutes. | Condition of heat. | Ag as Ag$_2$O. Per cent. |
|---|---|---|---|---|---|
| 1. | 0·5 | 2·5 MnO$_2$ | 60 | Medium | 9·40 |
| 2. | 0·5 | 5·0 MnO$_2$ | 60 | ,, | 7·78 |
| 3. | 0·5 | 2·5 Fe$_2$O$_3$ | 60 | ,, | None |
| 4. | 0·5 | 2·5 Bi$_2$O$_3$ | 60 | ,, | ,, |
| 5. | 0·5 | 2·5 ZnO | 60 | ,, | ,, |
| 6. | 0·5 | 2·5 CaCO$_3$ | 60 | ,, | ,, |

From the above it will be seen that silver oxide was produced, and remained as such where manganese dioxide was used, and in no other case ; it would also seem that this oxide was made at the expense of the manganese dioxide, and not by atmospheric oxidation, nor does it seem to have been produced in Experiment 3 (certainly not remaining as such), assuming the possible conversion of Fe$_2$O$_3$ to Fe$_3$O$_4$ (*Journ. Chem. Soc.*, lxv., 313).

TABLE B.

| No. of expt. | Ag in grm. | Heated with— Grms. | Time of heat. Minutes. | Condition of heat. | Ag as Ag$_2$O. Per cent. |
|---|---|---|---|---|---|
| 7. | 0·5 | 7·5 MnO$_2$ | 30 | Medium | 34·16 |
| 8. | 0·5 | 10·0 MnO$_2$ | 30 | ,, | 18·84 |
| 9. | 0·5 | 3·0 CaCO$_3$ | 60 | ,, | None |
| 10. | 0·5 | 3·0 Fe | 60 | ,, | ,, |

The above results show that silver oxide was produced in the presence of manganese dioxide only; that less duration of heat than in Table A gives the amazingly large per cent of that oxide, and it furthermore seems that the oxide produced is not in proportion to the manganese dioxide used, but the reverse condition is generally seen in each set of experiments.

TABLE C.

| No. of expt. | Ag in grm. | Heated with— Grms. | Time of heat. Minutes. | Condition of heat. | Ag as Ag$_2$O. Per cent. |
|---|---|---|---|---|---|
| 11. | 0·5 | 1 MnO$_2$ | 2·5 | High | 32·24 |
| 12. | 0·5 | 2 MnO$_2$ | 2·5 | ,, | 34·28 |
| 12. | 0·5 | 2 MnO$_2$ | 20 | ,, | 11·72 |

The above experiments show, other conditions being the same, the longer the duration of the heat the less oxide there is produced.

TABLE D.

| No. of expt. | Ag in grm. | Heated with— Grms. | Time of heat. Minutes. | Condition of heat. | Ag as Ag$_2$O. Per cent. |
|---|---|---|---|---|---|
| 14. | 0·5 | 5 PbO | 10 | Medium | 38·85 |
| 15. | 0·5 | 4 PbO$_2$ | 10 | ,, | 35·12 |
| 16. | 0·5 | 2 BaO$_2$ | 5 | ,, | 12·28 |
| 17. | 0·5 | 7 BaO$_2$ | 10 | High | 2·04 |
| 18. | 0·5 | 4 CuO | 12 | ,, | None |

In Nos. 14 and 15 the mixtures were placed in scorifiers, and covered with 10 grms. of lead oxide.

In Nos. 16 and 17 the mixtures were placed in cupels and covered with 2 grms. of barium dioxide.

It is interesting here to notice that barium dioxide serves as an oxidising agent ; that the amount of silver oxide produced decreases probably both with increase of time and temperature.

Although lead dioxide may readily give up a part of its oxygen, and thereby be converted into a lower oxide, yet the amount of silver oxide produced was no greater than with lead oxide alone; this is an interesting illustration of the property of lead oxide to serve as a possible carrier of atmospheric oxygen, producing silver oxide in a manner similar to that of the two bodies, manganese dioxide and barium dioxide, liberating oxygen. In the case of lead oxide, No. 14, if dissociation is not possible (*Journ. Chem. Soc.*, lxv., 316) even at so high a temperature as 1750° C., it seems most reasonable to account for its peculiar oxidising action, as mentioned above, viz., as a carrier of atmospheric oxygen. Although copper oxide has been shown to yield up a part of its oxygen at 1500° C., yet I find no evidence of silver oxide existing in Experiment 18 in the remaining ignited mass.

TABLE E.

| No. of expt. | Ag$_2$O in grm. | Heated with— Grms. | Time of heat. Minutes. | Condition of heat. | Ag as Ag$_2$O. Per cent. |
|---|---|---|---|---|---|
| 19. | 0·5 | 5 MnO$_2$ | 60 | Medium | 36·4 |
| 20. | 0·5 | 3 Fe | 60 | ,, | 0·3 |
| 21. | 0·5 | 3 CaCO$_3$ | 30 | ,, | 0·2 |

In Table E a variation was made in the nature of the experiment. Freshly prepared silver oxide was used; while this oxide was completely decomposed upon being heated gently upon a porcelain lid; yet in No. 19, where manganese dioxide was used, it will be seen that 36·4 per cent of this silver oxide completely escaped decomposition.

The above results, in connection with others along a similar line, have induced me to believe that attention has not heretofore been directed to the ease with which silver may be oxidised by lead oxide, and particularly by substances which give up a part of their oxygen upon gentle ignition, such as manganese dioxide and barium dioxide. Is it not, then, reasonable to assume that certain losses, or irregularities in the treatment of silver and its compounds, may be due to this cause?—*Journal of the American Chemical Society*, xviii., No. 3.

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## AN IDEAL CHEMICAL LABORATORY.*

### By Professor W. RAMSAY, F.R.S.

THE honour which has been done me in asking me to address you at the opening of these splendid new laboratories affords me an opportunity of making some remarks of a general nature on the use of a laboratory both to teachers and students. I entertain some very positive opinions on some matters connected with laboratories, partly based on innate conviction, partly on experience; and opinions, like clothes, require an airing occasionally, if only to preserve them from becoming moth-eaten, and to show where patches are required.

To begin, then, I hold that a laboratory should not be too large. You will in these days of exact Science, when mathematics invades even the microscope of the zoologist, request me to place an exact numerical value on the word "too." I will gladly do so. Too large means capable of containing more than forty or fifty students. But why not? Because students are, after all, human beings, and I do not believe that it is possible for any man to be interested in more than forty or fifty human beings all engaged in similar work. In the first place, it is difficult to remember the names of fifty people, and still more difficult to gauge their mental characteristics and be lenient to their mental aberrations. For this reason I prefer the number 40 to the number 50. One feels more at home with 40 than with 50 people. I should be still more pleased with 30, if they all were of sufficiently good calibre.

Of course it is as easy to lecture to five hundred as to fifty. And if, as in the old days, it were deemed sufficient for any one, designing in later years to be a barrister, a ship-builder, or an architect, that he should attend only lectures on chemistry, and not attempt laboratory work, and if it were the custom as in old days, not in order to prepare for any examination, but to acquire some knowledge of a subject, then we might be happy with lecture classes of any number capable of being reached by the human voice, and with laboratories filled with the *élite* of those classes; but now, when practical manipulation is required of every one who attends lectures, our lectures and our laboratories must, I suppose, be attended by the same—or by nearly the same—number of people. Hence if the laboratory is designed to hold forty, and only forty people, it is probable that our lectures, at least the general course, will be attended by the same number.

But what about assistants? Can they not, and do they not, bear the heat and burden of the day, contenting themselves with the skim-milk, and leaving the cream to the professor? To be sure they do; but that does not touch the fringe of the matter. For I hold it to be the professor's duty (and his privilege) to know reasonably well each one of his flock: to borrow a simile—the food must be prepared by the cooks (I do not use this word in the technical sense which it bears in chemistry), and the physician must see that it is being digested, and when necessary administer aperient pills. In plain language, the professor must know what each man is doing, and whether he is doing it well.

Among the forty or fifty, supposing them to be equally divided over a three years' course, there will be ten or twelve who are reasonably well acquainted with analytical operations, who have made a sufficient number of preparations, and have acquired manipulative skill. Such men are anxious to advance the bounds of Science. Having for more than two years watched the fabric of chemistry growing under the architectural operations of the professor and his assistants, and of others, their seniors in academic life, who have entered the temple of research, they yearn and burn to follow such enticing examples. But they are as yet not sufficiently fertile in ideas. Sometimes, of course, a young and inexperienced student conceives great thoughts; but such persons are rare. It is necessary, therefore, that the impulse be given from without; that some bricks be added to the temple of knowledge, to fill up gaps left by the carelessness or too great hurry of former builders; or that long neglected dust-heaps be swept out in the hope of discovering hidden treasure. It is the duty and privilege of the professor to call attention to these *lacunæ* and *thesauri*, and to suggest means whereby the former may be bridged and the latter recovered. Now it is not easy for any one man to supply mental material to more than a very limited number of researchers or to keep clearly in his mind the details of many pieces of work. It is like playing ten games of chess blindfold, only considerably more difficult. True, the player can see the board, by cross-questioning the players as to their movements; but the power of independent motion of the pieces, and the unforeseen nature of the combinations, complicates the nature of the problems. Moreover, it is a game where the pieces are being continually shifted by outsiders who publish their moves, and it is necessary to pay attention to such changes. In short, it is difficult enough to carry out one research at a time; it is supremely difficult to superintend a dozen. Hence another reason for the limitation of numbers.

But there is still another. In a comparatively small laboratory an atmosphere of interest exists. The workers speak to each other in friendly intercourse, and criticise each other's work. The influence of seniors on juniors is felt. But in a large laboratory, where the principles of the factory supersede the kindly intercourse of friends,—where one is lost in labyrinths of passages, and puzzled by multiplicity of rooms,—where no one knows what his neighbour is doing, nor cares, such advantages are lost. For my part I prefer the gossip of a village to the County Council formalities of a city.

Lastly, in a larger laboratory, there is need of organisation. The chief, that is the professor, is busied in administration. Apparatus to be ordered; servants to be superintended and paid; students to be enrolled and registered; correspondence to be conducted — all this takes time, and takes time from one whose time should be otherwise spent. And these are duties which cannot be delegated; to be well done, they must be done by the chief; and the chief should be engaged in the duties I have specified before. These are pleas for not too large laboratories.

I will now advance a plea for a not too luxurious laboratory. I do not advocate a reversion to the kitchen of Berzelius, or to the still more compact tray of bottles, pipestems, and candles of Wollaston, but I maintain that Heaven helps those who help themselves. To begin in the lap of luxury leads to effeminacy and incapacity. I can imagine a latter-day student, plunged in the penury of a works laboratory, weeping because no sulphuretted hydrogen is laid on; because to obtain steam he has to

boil water; because a vacuum cannot be obtained without manual labour. As an engineer should be able to make his own tools, so should a chemist; starting with glass tubes he should be able to extemporise a blowpipe, and make the most complicated apparatus. He should be a reasonably good gas-fitter and turner; he should be able to solder a joint; and he should be able to turn to account almost every apparently useless article. Faraday's chemical manipulation is a storehouse of hints, but we have added to his store. Now if the student has a shop at the corner, where all possible things may be procured; if he works in a laboratory where he has merely to turn a stopcock and results pour out, he loses by not having passed through the ordeal of hard experience. A little time is lost; but here loss of time means gain in almost every other respect.

One word about the teaching of students. The theme of chemical education has been recently discussed within these walls, but on totally different lines from those which I propose to follow. My thesis here is that students are as a rule much overtaught. I should not regard that laboratory as a chemical heaven where every student had an assistant at his elbow, keeping him in the straight path, and guarding him from error. And taking for granted that the object in training students in chemistry is to teach them to discover new truths, and to form theories concerning the relations between old truths, it is best to adopt the well known method of trial and failure. A student gains much more knowledge, much more experience, and much more confidence, if, instead of following a printed guide, he attempts, *propriæ motu*, to devise a new method (even when its failure stares in his teacher's face) and tries it. Indeed, there is far too much spoon-feeding. The frequent elementary treatises which supply "a long-felt want," and which repeat the boiled-down truisms of chemistry, are much on a par with the widely advertised foods for infants. Let the student, as far as possible, be left to devise his own processes and his own instruments, adapting to his immediate use what he finds in the laboratory; for that is what he ultimately will have to do when he starts for himself. There are two reasons which argue in favour of this course; it is much more beneficial for the student, and it is much less arduous for the teacher. Of course, like everything else, this process may be carried too far, but let the help be given as help, and not as a set of methods and rules. The one method of teaching turns out competent investigators; the other, competent workmen. But it is investigators that we should manufacture in such laboratories as this.

One word more and I have done. What is it that gains a student a position in making a start in the world? Is it a high degree? Not unless he wish to start as a schoolmaster, and then a competent knowledge of, and an intense interest in, the games of football and cricket are held in as high esteem. It is the good word of his teacher. And why do his teachers thus recommend him? Because they have studied and valuated his character during the years of intercourse. That is the examination through which we all have to pass; a practical examination which lasts a lifetime. Would it not be well to award our science degrees by what, after all, is the only criterion of merit in the world, the judgment of those of our fellows capable of forming an opinion?

Many of those I am now addressing will follow a career in technical chemistry. For such, a knowledge of methods is indispensable. Engineers should work hand in hand with chemists; for many chemical processes depend for their success on the smooth working of the plant by which they are realised on a large scale. What yields good results with a grm. often fails with a thousand kilogrms., owing to difficulty of treatment, which means expense.

But I do not think that it is advisable for young chemists to carry out experiments *en gros*; for first, it is a very expensive amusement, and second, as far as chemistry is concerned, little is learned. But here again the happy mean must be sought. It is useful occasionally to attempt to carry out operations in iron and stoneware vessels on perhaps a kilogrm. of material, so as to learn the different methods of treating small and comparatively large quantities of material.

The donors of this magnificent laboratory are men who have spent their lives in putting chemical theory into practice. As you know, Mr. Gossage and Mr. Timmis have raised this building in memory of Mr. William Gossage, the father of the former, and a great inventor in his day; and Sir John Brunner, Mr. E. K. Muspratt, and Messrs. Lever Brothers have aided most generously in providing necessary rooms. These are names which stand in the forefront of our chemical industry, and the history of the alkali trade in future years will rank their achievements on a par with the landing of Julius Cæsar, or the reign of King Alfred. It is to Mr. William Gossage that most of the important features of the alkali trade are due; for example, the condensation of hydrochloric acid, instead of allowing it to escape to pollute the air; the smelting of pyrites residues for copper; the utilisation of caustic mother-liquors of soda-crystals for the manufacture caustic soda, and the utilisation of sulphur waste. But it is not my function here to enter into chemical details; I mention Mr. Gossage's name, and those of the other donors of these laboratories, in order that I may point to them as chemical products of a very high order, and invite those of you who are to make use of their magnificent donation, to follow in their footsteps, proving yourselves able to advance science, and to benefit your fellow creatures.

## LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
*Water Examiner, Metropolis Water Act*, 1871.

London, December 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 2nd to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined all were found to be clear, bright, and well filtered.

The rainfall at Oxford during November again shows a serious deficiency, after an excess of 3·14 inches for the two previous months. The average fall for November is 2·42 inches, while the actual fall was 0·79, showing a deficiency of 1·63 inches, bringing the total deficiency for eleven months of the year to 4·46 inches, or about 20 per cent.

The numbers of microbes in the waters is keeping satisfactorily low. The following table shows our results:—

| | Colonies per c.c. |
|---|---|
| Thames water, unfiltered .. .. .. .. .. | 2223 |
| Thames water, from the clear water wells of the five Thames-derived supplies.. highest | 62 |
| Ditto ditto .. .. .. .. lowest | 4 |
| Ditto ditto .. (12 samples) mean | 21 |
| New River water, unfiltered .. .. .. .. | 1054 |
| New River water, from the Company's clear water well .. .. .. .. .. .. .. .. | 20 |
| River Lea water, unfiltered .. .. .. .. | 1178 |
| River Lea water from the East London Company's clear water well .. .. .. .. .. | 6 |

These figures prove the excellence of the Companies' filtering and storage appliances.

Having had our procedure attacked, we may as well put on record that since commencing the bacterial examination of the London waters in 1886, we have *always* used incubators properly controlled by sensitive gas regulators, and in no instance has the internal temperature varied beyond the proper limits, namely, in the case of gelatine cultures, between 20·0° and 20·5° C. To our surprise, however, in Dr. Klein's recent report to the London County Council he expresses himself in the following words :—

" I have seen it stated in the publications of the London Water Companies' analysts that during November these gentlemen counted the colonies, after forty-eight hours, in the plates *exposed to the ordinary temperature of the laboratory*, and found their numbers varying between seven and seventy. I have no hesitation in saying that no bacteriologist would accept these figures as representing the actual number of bacteria present in the water; only a fraction of the colonies develop in a gelatine plate after forty-eight hours if the plate is kept at temperatures below 17° or 18° C."

Further on Dr. Klein says :—

" The small number of microbes stated to be present in the London waters by the Companies' analysts are only to be explained by the imperfect methods used, *keeping the plates at the temperature of the laboratory*, and counting the colonies already after forty-eight hours, when they have barely commenced to grow." (The italics are ours).

Now, it will scarcely be believed that the above-quoted assertions, which Dr. Klein has made for the purpose of throwing discredit on our bacteriological results, have no foundation in fact. In none of our reports have we ever made any such statement.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

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## THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.*

### By L. M. DENNIS.

SOME time ago the author and F. L. Kortright (*Ztschr. Anorg. Chem.*, vi., 35 ; *Am. Chem. Journ.*, xvi., 79) briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been possible to prepare an amount of the reagent sufficient for the investigation described below.

The solution of potassium trinitride which was used was prepared by carefully neutralising a dilute solution of hydronitric acid with a dilute solution of pure caustic potash and then adding hydronitric acid sufficient to give to the solution a distinctly acid reaction. The solution first employed contained about 3 2-10 grms. of potassium trinitride to the litre.

Before studying the separation of thorium from the other rare earths, the reaction between potassium trinitride and pure thorium chloride was first investigated. The thorium employed was from a sample of thorium oxalate, which had been very kindly presented to me by Dr. Theodor Schuchardt, of Goerlitz. It was found to be of a very high grade of purity, but to guard against the possible presence of other rare earths, the oxalate was converted to the oxide by ignition, treated with concentrated sulphuric acid, the anhydrous sulphate dissolved in distilled water at a temperature of 0°, and this solution was precipitated with pure oxalic acid. The precipitated thorium oxalate was thoroughly washed with hot water containing 1 per cent hydrochloric acid, and was then dropped into a hot concentrated solution of ammonium oxalate. It dissolved completely, and no precipitate formed when the solution was diluted and cooled. From this solution the thorium was again precipitated as oxalate by means of strong hydrochloric acid, and was then brought into solution as thorium sulphate in the manner described above. It was then precipitated by ammonium hydroxide, and the precipitate thoroughly washed with water. The thorium hydroxide was then dissolved in hydrochloric acid, ammonium hydroxide was added until a faint but permanent precipitate remained, and this was then removed by filtration. There was thus obtained a neutral solution of thorium chloride containing a very small amount of ammonium chloride.

The strength of this solution of thorium chloride was ascertained by precipitating portions of 10 c.c. each with ammonium hydroxide, filtering, washing, igniting, and weighing as $ThO_2$. Two determinations gave for thorium oxide in 10 c.c., 0·0591 grm. and 0·0595 grm. The mean of these results is equivalent to 0·00521 grm. thorium in 1 c.c.

Upon adding to this thorium solution a few c.c. of the solution of potassium trinitride, the precipitate which, in the previous work with Dr. Kortright, had formed at once, failed to appear; upon heating the solution to boiling, however, there was quickly formed a white flocculent precipitate, closely resembling in appearance aluminum hydroxide, but settling rapidly when the flame was removed. In the first determinations the solution was boiled for five minutes, but it was later found that boiling for one minute is sufficient. During the boiling the odour of hydronitric acid was distinctly noticeable. The precipitate was washed by decantation with hot water, transferred to the filter, ignited, and weighed as $ThO_2$. Twenty c.c. of thorium chloride, containing, according to the determination with ammonium hydroxide, 0·1186 grm. thorium dioxide, gave, by precipitation with potassium trinitride, 0·1183 grm. thorium dioxide, equivalent to 0·00520 grm. thorium in 1 c.c. instead of 0·00521 as obtained with ammonia.

It is apparent, therefore, that thorium can be quantitatively precipitated by potassium trinitride.

The previous work of Dr. Kortright showed that the thorium is probably precipitated as the hydroxide, but the tendency of the precipitate to absorb carbon dioxide rendered the analyses unsatisfactory. If, however, the thorium is precipitated as the hydroxide, then all of the hydronitric acid of the potassium salt first added must reappear in the filtrate from the thorium hydroxide and in the gas evolved during the boiling. To ascertain whether this took place the precipitation was made in a round bottomed flask. In the neck of the flask there was inserted a two-hole rubber stopper, through one

opening of which a current of purified air was admitted, the other opening carrying an upright condenser. The condenser was connected at the upper end with two absorption vessels containing neutral silver nitrate solution. As the hydronitric acid was to be determined by precipitation with silver nitrate, a neutral thorium nitrate solution, containing 0·0075 grm. thorium in 1 c.c., was substituted for the thorium chloride. The thorium nitrate solution was placed in the flask, potassium trinitride was added, and after starting a current of air through the apparatus, the contents of the flask was heated to boiling and kept boiling for two minutes. Soon after the heating began a white precipitate of silver hydronitride formed in the first absorption flask containing the silver nitrate; by the time the reaction was complete this precipitate had become quite voluminous. The absorption of the gas by silver nitrate seems to be both rapid and complete, for nothing more than a slight opalescence ever appeared in the second absorption flask. After the apparatus had become cool the thorium hydroxide was filtered off, and the filtrate was precipitated by silver nitrate. The silver trinitride thus obtained, together with that in the absorption flasks, was washed by decantation with cold water, the washings being passed through a hardened filter. When the wash water gave no further reaction for silver, the funnel with the filter was placed in the neck of the flask containing the main part of the precipitate, and quite dilute hot nitric acid was poured upon the paper. The silver trinitride on the paper dissolves almost immediately. After washing the paper with water, the funnel was removed, and the contents of the flask was boiled until all of the silver trinitride had dissolved. The silver was then precipitated by hydrochloric acid and weighed as silver chloride. Ten c.c. of thorium nitrate and ten c.c. of potassium trinitride were used. The silver chloride resulting weighed 0·1447 grm. equivalent to 0·0434 grm. hydronitric acid. The strength of the potassium hydronitride, which was a different solution from the one first employed, was then determined in the same manner.

5 c.c. gave 0·0744 AgCl = 0·02232 HN₃,
5 c.c. gave 0·0745 AgCl = 0·02235 HN₃.

Using the mean of these results, it appears that 0·0446 grm. of hydronitric acid was used in the precipitation of the thorium nitrate, of which 0·0434 grm. was recovered from the filtrate and distillate. That this latter result is somewhat low is doubtless due to the loss of hydronitric acid by volatilisation during the filtration of the liquid in the flask. These results, together with those given in the preceding article already referred to, enable us to represent the reaction by the equation—

$$Th(NO_3)_4 + 4KN_3 + 4H_2O = Th(OH)_4 + 4KNO_3 + 4HN_3.$$
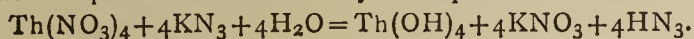
This reaction is interesting not only because of the quantitative precipitation of thorium by this means, but also because of the peculiar behaviour of the potassium hydronitride. As Ostwald has stated, hydronitric acid is but slightly stronger than glacial acetic acid, and the above equation reminds one of the behaviour of acetates towards ferric iron, the solution of ferric acetate being fairly stable in the cold, but breaking down upon heating into acetic acid and ferric hydroxide.

The experiments detailed below were then made to ascertain whether thorium could be quantitatively separated from the other rare earths by means of the above reaction. A neutral solution of pure lanthanum chloride was first prepared, and its strength determined by precipitating with ammonium hydroxide and weighing the lanthanum as $La_2O_3$. The solution contained 0·00431 grm. lanthanum in 1 c.c. This solution gave no precipitate when boiled for some minutes with potassium trinitride. 15 c.c. of this solution and 15 c.c. of the thorium chloride solution were placed in an Erlenmeyer flask, 25 c.c. of potassium trinitride ($3\frac{2}{10}$ grms. to the litre) were added, and the solution was boiled for one minute. The precipitate was filtered off and washed with hot water, ignited, and weighed. To the filtrate 5 c.c. more of potassium

trinitride was added, and the solution boiled for two minutes. No further precipitation resulted. The solution was then precipitated with ammonia, and the lanthanum weighed as the oxide. The results were:—

|  | Taken. | Found. |
|---|---|---|
| Thorium .. .. | 0·0781 | 0·0777 |
| Lanthanum . .. | 0·0646 | 0·0642 |

A mixture of the rare earths in Brazilian monazite was then freed from thorium by repeatedly digesting the mixed oxalates with a hot concentrated solution of ammonium oxalate. The residual oxalates were then transformed into chlorides and dissolved in water. The solution showed the pink colour and absorption bands of didymium, and gave a strong reaction for cerium when treated with hydrogen peroxide and ammonia. When boiled with potassium trinitride it gave a very faint precipitate, which was filtered off. By precipitation with ammonia, this solution of cerium, lanthanum, didymium, &c., free from thorium, was found to contain 0·0166 grm. of the mixed oxides in 1 c.c. The precipitation was made as in the separation from lanthanum, and an excess of potassium trinitride was used in each case.

|  |  | Taken. | Found. |
|---|---|---|---|
| I. | Thorium .. .. .. .. | 0·1300 | 0·1294 |
|  | Ce, La, Di oxides .. .. | 0·0332 | — |
| II. | Thorium .. .. .. .. | 0·0785 | 0·0783 |
|  | Ce, La, Di oxides .. .. | 0·0830 | — |
| III. | Thorium .. .. .. .. | 0·0535 | 0·0526 |
|  | Ce, La, Di oxides .. .. | 0·2490 | — |
| IV. | Thorium .. .. .. .. | 0·0535 | 0·0531 |
|  | Ce, La, Di oxides .. .. | 0·2490 | — |
| V. | Thorium .. .. .. .. | 0·0550 | 0·0541 |
|  | Ce, La, Di oxides .. .. | 0·4980 | — |
| VI. | Thorium .. .. .. .. | 0·0555 | 0·0550 |
|  | Ce, La, Di oxides .. .. | 0·5810 | — |
| VII. | Thorium .. .. .. .. | 0·0570 | 0·0558 |
|  | Ce, La, Di oxides .. .. | 0·8300 | — |

The recovery of the thorium is in all cases fairly exact, and the variation in the relative amounts of thorium and the other earths does not influence the sharpness of the separation. That thorium alone is precipitated by potassium trinitride is to be explained by its weak basicity. It is the weakest base in the whole group of the rare earths, with the possible exception of cerium in the ceric condition, and this higher form of cerium is probably incapable of existence in the presence of hydronitric acid.

We have, then, in potassium trinitride a reagent which can be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. So far as the author is aware, this is the only method as yet devised by which one of these earths can be quickly and accurately separated from the others, and that in a single simple operation.—*Journal of the American Chemical Society*, xviii., No. 11.

Society of Arts —At the meetings of the Society of Arts after Christmas the following papers will be read :—"The Roller Boat of M. Bazin," by Emile Gautier; "Voice Production," by William Nicholl; "Irish Industries," by the Hon. Horace Plunkett; "English Orchards," by George Gordon; "The Prevention of Fires due to Leakage of Electricity," by Frederick Bathurst; "Dairy Produce and Milk Supply," by M. J. R. Dunstan. M.A. ; "The Transmission of Power by Alternating Electric Currents," by W. B. Esson, M.Inst.C.E. ; "London Water Supply," by Percy F. Frankland, Ph.D., F.R.S. ; "The Chemistry of Tea," by David Crole ; "The Evolution of the Silver Question," by Moreton Frewen, B.A. ; "Children's Sight," by R. Brudenell Carter, F.R.C.S. ; "Light Railways," by Everard C. Calthrop; "Cycling—Historical and Practical," by George Lacy Hillier.

# PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

*Ordinary Meeting, December 3rd, 1896.*

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 393).

164. "*The Oxidation of Ferrous Sulphate by Sea-water, and on the Detection of Gold in Sea-water.*" By E. SONSTADT.

The experiments now described were made in the autumn of 1895, on sea-water supplied by the Great Eastern Railway Company in oak kegs, freshly filled, the water being stored in glass bottles as soon as received, and filtered before use.

I. *On the Oxidation of Ferrous Sulphate by Sea-water.* —In 1872 (CHEMICAL NEWS, xxv., 196, 231, and 241) the author gave a description of experiments proving the existence in sea-water of calcium iodate, four parts of this salt being shown to be present in one million parts of sea-water. As these experiments have not, within my knowledge, been repeated, and as I do not know of any analysis of sea-water recognising the presence of any salt therein capable of acting as an oxidiser, it seemed desirable to make direct experiment on the oxidising power of sea-water. To do this satisfactorily, it seemed necessary to compare sea-water against sea-water so treated as to reduce any salts of the nature of iodates that it might contain, due care being taken to thoroughly aërate the treated portion.

*First Experiment.*—1½ lbs. sea-water were evaporated to dryness with a small quantity (about 2 grms.) of pure mercury, and the residue was heated in a porcelain crucible into which a current of hydrogen was passed, until the mercury was completely expelled. The salts were digested in water, and the solution made up by washings to the original quantity. The solution was then put into a Winchester quart bottle, and repeatedly shaken up, the air being renewed from time to time. When it was judged that the aëration was complete, one pint of the solution was put into a bottle which it nearly filled, and 1 grm. of crystallised ferrous sulphate was added. A pint of the original sea-water was put into another similar bottle, with the same quantity of ferrous sulphate, and 1¼ c.c. of dilute hydrochloric acid was added to each solution. The bottles were corked, and, after sufficient shaking to ensure mixture, were set side by side for three days, when the contents of both bottles were filtered simultaneously. After washing the precipitates with equal quantities of water, drying, and ignition, the ferric oxide from the natural sea-water weighed 0·0182 grm., and that from the treated sea-water 0·0132 grm.

*Second Experiment.*—This was conducted similarly to the first experiment, except that instead of evaporating the sea-water, with mercury, the latter was rubbed up with the residue left after drying, the subsequent heating in a current of hydrogen being conducted as before. Also, no acid was added to either the natural or the treated sea-water, and, after the addition of ferrous sulphate, the solutions were allowed to stand in the corked bottles for thirteen days before filtering. The natural sea-water gave ferric oxide 0·0540 grm. (after solution and re-precipitation 0·0528 grm.), and the treated sea-water 0·0270 grm. Thus the difference in this case, when no acid was added, and more time was allowed for the formation of the precipitates, was very much more than in the first experiment, and is greatly in excess of what can be due to the influence of the iodate present in the untreated sea-water.

Although in these experiments it was found impossible to completely dissolve the salts obtained after ignition, in the quantity of water required to form an equal volume with the original sea-water taken, yet there is no reason-able ground for supposing that the change in composition thus effected could sensibly affect the oxidising power, apart from the reduction involved of the iodate, and other salts at present unrecognised, of a reducible character. The insoluble residue contained traces of several metals, all of which were not definitely recognised, an account of which I defer until an opportunity occurs to me of working upon larger quantities of material.

II. *On the Detection of Gold in Sea-water by means of Mercury.*—About 20 grms. of pure mercury was agitated in a flask with about half a gallon of sea-water for a long while, the flask being placed at intervals on a water-bath, so that the liquid became warm, though not hot. In subsequent experiments the water was not warmed, and no special proportion of mercury was used, though obviously the smaller the proportion of mercury the more agitation would be necessary to obtain the same result. The mercury was separated, washed, and dried with bibulous paper. The mercury was then volatilised in a porcelain crucible having an uninjured internal surface. A black adherent film remained, fixed at a red heat. When the crucible had cooled, a small quantity of strong hydrochloric acid was added, which, on warming, dissolved the greater part of the film, leaving, however, a stain not removable by repeated similar treatments. The acid solution being washed away, and the crucible dried, a drop or two of aqua regia was let fall on the stain, which was almost immediately dissolvsd. By cupellation a very minute gold bead was obtained. In some experiments the mercury that had been agitated with sea-water was distilled in a current of hydrogen, but on afterwards heating the black residue in the porcelain boat, in the open air, the residue was not adherent, and could not therefore be treated as described. To obtain an adherent film, 4 to 5 grms. of mercury must be left for volatilisation in the open. The mercury that is distilled off in a current of hydrogen is quite pure; but that volatilised in contact with air is not pure, for if a portion of it be condensed on a cool surface, and then volatilised, a residue remains which disappears on strong heating. Silver is one of the metals dissolved out from the black residue by the hydrochloric acid with which it is treated. This fact, although somewhat outside the subject of the present paper, is worth mentioning, as having a bearing upon the question as to the condition in which the precious metals are present in sea-water. Mercury does not decompose silver chloride, either in the wet or dry way, and yet it separates silver from sea-water. The most natural inference appears to be that the silver salt in sea-water is so far attenuated by dilution as to have undergone molecular disruption, so that it may be considered to be present as metallic silver in solution. If this be so in respect to silver, the gold in sea-water is probably also in a similar condition.

A comparison cannot be instituted between the simple and easy process now described, for detecting the presence of gold in sea-water, and the processes given in the author's paper "On the Presence of Gold in Sea-water" in 1872 (CHEM. NEWS, xxvi., 159), because the sea-water that comes in kegs from the sea-side is very much poorer in gold than the water of the Irish Sea, on which the author's earlier experiments were made. When some gallons of sea-water, furnished by the Great Eastern Railway Company, were heated with ferrous sulphate and a little hydrochloric acid, and the precipitate, after a few days, collected, the minute gold bead from this precipitate (which was lost by accident before it could be weighed) was certainly but a small fraction of what the same quantity of sea-water previously experimented upon would have yielded. Whether this poverty in gold of the keg-water is due to its brief contact with wood, or to the circumstance that it is taken from shallow water near the shore, where a certain admixture with mud or clay is inevitable, may be doubtful. But it is probable that finely divided clay, mixed with sea-water, would carry down with it, in settling, most of the gold present.

## NOTICES OF BOOKS.

*Select Methods in Inorganic Quantitative Analysis.* By BYRON W. CHEEVER, A.M., M.D. (late acting Professor of Metallurgy in the University of Michigan). Third Edition, revised and enlarged, by FRANK CLEMENT SMITH, B.S., E.M., Professor of Geology, Mining, and Metallurgy, State School of Mines, Rapid City, S.D. Edinburgh: W. F. Clay, 18, Teviot Place. 8vo., pp. 154. 1896.

THIS able work, although published in Edinburgh, has evidently been written in America, and with a reference to American conditions. Thus we find tables for the use of Baumé's hydrometer, and mention of "casseroles" as vessels in which to effect solution in acids.

The work does not include in its scope all classes of inorganic substances. The substances omitted are of little practical or commercial moment, but their unexpected occurrence may complicate the procedure required and lead the student astray. Among the poisonous metals which may possibly occur in the waste waters of industrial districts, are those especially where dyeing is carried on on a large scale.

By a printer's oversight, the capacity of the British gallon has been given as 7000 fluid grains. In all the substances touched upon the instructions given are not only accurate but full.

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*Treatise on Distillery: Industries of Distillation, Ferments, and Alcohols.* ("Traité de Distillerie: Industrie de la Distillation, Levures, et Alcohols"). By M. P. GUICHARD, Member of the Chemical Society of Paris. Paris: J. B. Baillière et Fils. Pp. 388.

THIS work is one of the valuable series of scientific and technical treatises issued by the firm of J. B. Baillière and Sons. The subject is one which has attracted much thought and attention in France since the vineyards of that country have been ravaged by the phylloxera. We cannot help pointing out that when that scourge first invaded France, some of the leaders of the "Temperance" movement openly rejoiced in the delusion that the result would favour their cause. But, alas! the amount of alcoholism in France has not decreased since the destruction of so many vineyards.

Alcohol, of a sort, is manufactured from a variety of other substances. There are alcohols distilled from potatoes, from beet-root, from beet-root treacle, from Jerusalem artichokes, &c., &c.

The author expresses his gratitude for the fact that France is not exposed to the inroads of whisky. So be it, but we may in turn rejoice that we are as yet exempt from potato-whisky—the scourge of North Germany,—and from absinthe, the most deleterious of all spirituous liquors.

M. Guichard treats first of the manufacture of saccharine liquids, by the agency of malt and by acids, and on the fermentation of different classes of substances.

He then proceeds to the industry of ferments, an art in which France has been of late eminently successful. Next we come to the manufacture of alcohol and its purification.

On the use of alcohol as a drink the author takes a stand which we think will prove almost, if not entirely, satisfactory to the shade of the late Sir B. Richardson. He contends that alcohol is not a food, there being no true foods but substances which enter into the constitution of our body, and he gives tables showing the proportion of impurities contained in different ardent spirits. It would appear that the first and most costly Cognacs are often less pure than the "industrial alcohols." Among the more dangerous liquors he classes not only absinthe and vermouth, but anisette and chartreuse! Pure alcohol he admits, however, is five times less dangerous than the essences which it contains.

A useful appendage is the vocabulary of the French, English, and German terms for the substances, the plant, and the operations occurring in the distiller's business. Unfortunately the English equivalents for French and German terms are largely incorrect.

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*Exercises in Practical Chemistry, mostly Quantitative; being the Appendix to " Chemistry for Beginners."* By R. L. TAYLOR, F.I.C., F.C.S. London: Sampson Low, Marston, and Co., Ltd.

THIS is one of that ever-numerous class of books in which we can find nothing to blame, and at the same time are at a loss to recognise a *raison d'être*. We can only hope that some day the beginners will reach maturity, and pour upon us a flood of results.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences.* Vol. cxxiii., No. 22, November 30, 1896.

**Scientific Exploration in Balloons.**—M. Mascart.—Already inserted.

**Determination of Nitric Acid in the Waters of the Seine, the Yonne, and the Marne, during the last Floods.**—Th. Schlœsing.—Already inserted.

**Absorption of Nitric Oxide by Ferrous Bromide** —V. Thomas.—Ferrous bromide in an aqueous solution absorbs nitric oxide according to the law of Gay-Lussac. In a future paper I shall show that the ethereal solution behaves quite differently, and that by suitable arrangements we may obtain a solid compound perfectly crystalline like the chloride.

**Tempering Steel with Phenic Acid.**—M. Lowat.—Steel tempered in phenic acid acquires hardness, elasticity, and suppleness.

**Action of Permanganate on the Polyatomic Alcohols and their Derivatives.**—L. Perdrix.—In general the products of the oxidation are formic acid and carbonic anhydride. To this rule the monatomic alcohols form exception.

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*Zeitschrift fur Analytische Chemie.*
Vol. xxxv., Parts 4 and 5.

**Detection and Determination of Sulphocyanogen in Technical Ammonium Sulphate.**— Offermann.— This process cannot be effected by means of ferric chloride in an aqueous solution. The solid salt must be extracted with alcohol. For the quantitative operation, 5 grms. of the salt are extracted for an hour with absolute alcohol, and the sulphocyanogen may be determined colorimetrically by comparison with a specimen of known strength.—*Apotheker Zeitung.*

**Determination of the Colouring Power of Litmus.**—E. Dieterich (*Helfenberg Annalen*).—Already inserted.

**Determination of Insoluble Residue in Isinglass.—** E. Dieterich.—Ten grms. of the material are cut into fine slips and boiled four times with 360 c.c. of water for fifteen minutes each time ; the residue is dried at 100° until the weight is constant.—*Helfenberg Annalen.*

**Distinction between Articles of Silver and of Nickel.** — The author uses a concentrated solution of silver nitrate. Genuine silver remains bright if moistened with the liquid ; spurious articles turn black. Lacquer, if present, must first be rubbed off. The writer mentions, also, the 10 per cent solution of chromic acid. A drop of this liquid produces on silver a purple-red spot, but on other metals (except gold and platinum) a greyish black.

**Sources of Error in the Assay of Gold and Silver.—** Farman.—From the *Engineer and Mining Journal.*

**Losses in the Cupellation of Bismuth-silver Alloys.—**E. A. Smith.—From the CHEMICAL NEWS.

**Determination of Silica in Blast-furnace Slags.—** P. W. Shimer.—The author evaporates down with sulphuric and hydrofluoric acids.—*Journal of the American Chemical Society.*

**Valuation of Manurial Matter containing Phosphoric Acid Insoluble in Water.—**E. Wrampelmeyer (Landwirth Versuchsstationen). — There appear no characteristic differences between basic slag meals and phosphorites on treatment with a 5 per cent solution of citric acid and acid potassium oxalate.

**Determination of Potassa in Manurial Salts.—**V. Edwards.—From the CHEMICAL NEWS.

**Determination of Yellow Phosphorus.—**Jal. Fóth (*Chemiker Zeitung*).—The author extracts with carbon disulphide until the extract, on shaking with silver nitrate, gives merely a faint brown colour.

**Ferropyrin.—**This is a proprietary medicine, made up by Knoll and Co., of 3 mols. of antipyrin and 1 mol. ferric chloride.

**Recognition and Determination of Mercury in Urine.—**A. Jolles.—The author uses metallic gold in the form of a powder in place of the materials previously used for amalgamation.—*Monats'hefte für Chemie.*

**Reaction for Acetacetic Acid in Urine.—**K. A. H. Mörner (*Skandinav. Archiv f. Physiologie*).—The urine is mixed with potassium iodide and ferric chloride. On boiling, a peculiarly irritating vapour is given off.

**Determination of Glucose.—**Lohnstein finds that the decrease of density on fermentation is not strictly proportional to the quantity of glucose.

**Conditions of Solution of Uric Acid in Urine.—** F. J. Smale (*Central-Blatt f. Physiologie*).—The author has obtained and examined saturated solutions of uric acid in water, in solution of sodium chloride, in solution of urea, and in solutions of disodium and monosodium-phosphate.

**Detection of Urotilin,** Jolles (*Pflüger's Archiv*) ; of hæmatoporphyrin in urine, Garrod (*Jour. of Physiologie*) ; and preservation of urinary sediments for microscopic examination (*Comptes Rendus*). We must refer to the originals.

**Atomic Weights of Cerium, Didymium, Lanthanum, and some other Rare Elements.** — P. Schützenberger (*Comptes Rendus*) has determined the atomic weight of cerium as 139·45. Brauner's method gave Ce=142—143. He gives the name meta-cerium to an element accompanying cerium and differing from it by a few spectral lines. Schützenberger calculates the atomic weight of didymium as 143—143·5. He succeeded in splitting up lanthanum into two earths having the respective atomic weights 138 and 135. From monasite he obtains the oxide of an earth forming salts of a full rose colour ; its absorption spectrum corresponded to that of neodymium, and its atomic weight was close upon 137·5.

## MISCELLANEOUS.

**University of Edinburgh Chemical Society.—**The second Ordinary Meeting of the above Society was held on Monday, December 14th. Dr. H. W. Bolam gave the Society an account of a research " On the Saponification of Dicarboxylglutaconic Ether " (see CHEMICAL NEWS, lxxiv., p. 278) ; a discussion took place after the paper had been read.

**The Light Rays of the Firefly** (Species ?) — Prof. Muraoko, a Japanese *savant*, has communicated to Wiedemann's *Annalen* the results of some observations made on the light emitted by the firefly. He finds that this light, if transmitted through black paper, acquires properties similar to those of the X rays. Like the Becquerel, they are intermediate between the X rays and the ultra-violet. The firefly rays are capable of reflection, but whether they are susceptible of refraction, polarisation, and interference, it has not yet been demonstrated.

**Cow Dung as a Cause of the Infection of Milk by Bacteria.—**W. W. Favra.—The connection of cholera infantum with the bacteria of milk is demonstrated. Flugger has especially referred to twelve kinds of bacteria which he has isolated which occur in market-milk, one of which peptonises casein strongly ; three of these species are strongly pathogenous. The author takes up the question of the introduction into considering the circumstance that, according to several investigations, from 3 to 19·7 m.grm. of impurities were found in milk which on microscopic examination are found to consist of particles of dung ; there were instituted a series of bacteriological investigations of cow-dung. In 0·001 grm. there were found as many as 20,000 aërobic bacteria. The anaërobic species and those which do not grow upon agar-agar we disregarded. From seven to eight distinct species were recognised. The majority belonged to the ordinary intestinal bacteria ; about 1½ per cent of all the bacteria were spores of peptonising bacteria. On a qualitative examination there were found four kinds of peptonising bacteria, I., VIII., IX., and XII. VIII. and XII. are especially of practical importance, as their spores are very persistent, and are not killed on boiling for four to five hours. The author believes therefore that cow-dung is one of the principal sources of the pollution of milk, especially on account of the peptonising and pathogenous bacteria. —*Wratsch*, 1896, xvii., 1114, and *Chemiker Zeitung*.

## MEETINGS FOR THE WEEK.

TUESDAY, December 29th.      ⎫ Royal Instituton, 3. (Christmas Lec-
THURSDAY, December 31st.    ⎬ tures). " Visible and Invisible
SATURDAY, Jan. 2nd, 1897.     ⎭ Light," by Prof. S. P. Thompson.

# INDEX.

END OF VOLUME LXXIV.